

# The carbonization of blends of pitches and resins to produce anisotropic carbon and the effects of pressure

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Selected pitches and resins were co-carbonized at atmospheric pressure and higher pressures to determine whether the addition of resin to pitch can improve the yield and modify the optical texture of the resultant carbon. Results indicate that some of the resins used can improve the yield and react with the pitch to produce a homogeneous, one-phase carbon in which the optical texture of the parent carbon has been modified. Resin/pitch blends which did not interact at atmospheric pressure show some interaction at higher pressures; pressure can thus be used to improve compatibility of blend components.

## 1. Introduction

Carbon composites are prepared industrially using a carbon fibre weave impregnated with a matrix precursor chosen for suitability of properties for the intended use of the composite. Pitch coke and other anisotropic carbon matrices are of use in, for instance, the aeronautic and aerospace industries where their high resistance to thermal shock and ability to survive at high temperature is of considerable importance [1, 2]. The yield of carbon from pitch is low unless special techniques such as high pressure carbonizations are used.

Composites prepared using a resin (e.g. phenol formaldehyde resin) as matrix precursor are lightweight and the resin gives a high yield on curing. They are, however, limited to lower temperature applications [3]. Interfacial stresses in the prepared composites are frequently induced because of shrinkage of the resin matrix and the difference in elasticity modulus between the matrix and reinforcing fibres.

There are many applications in modern industry where a combination of the properties of the two types of matrix would be advantageous. The possibility exists of combining the graphitic structure of pitch carbons with the higher yields from certain resins by use of a blend of resin and pitch as matrix precursor in carbon fibre com-

posites. The purpose of such a study would therefore be to determine the properties of carbons from the co-carbonization of pitches and resins. This is done by examining the polished surfaces of these carbons under a polarizing optical microscope to determine their optical textures [4]. These are compared with optical textures of carbons from parent pitch and resin. If pitch and resin do not interact on carbonization, a two-phase optical texture results in which the isotropic texture of the resin carbon and the anisotropic texture of the pitch carbon occur in sharply defined regions.

If the resin and pitch partly interact, these isotropic and anisotropic regions still occur but with a gradation of optical texture across the boundary between them. If they interact completely then a homogeneous anisotropic texture results which is not the same as carbon from the pitch carbonized singly, i.e. the resin modified the optical texture of the pitch carbon.

The objectives of this study are therefore to investigate the compatibility of certain pitches and resins on co-carbonization and to determine whether the addition of resin to pitch can improve carbonization yields of the pitch. The effects of pressure on the co-carbonization of resins and pitches are also investigated.

## 2. Materials used

### 2.1. Pitches

The following pitches were used:

Ashland A240 petroleum pitch,  
D112 coal extract,  
Esso CP1510 petroleum pitch.

### 2.2. Resins

The following industrial resins were used:

CS217,  
SC1008 resin,  
HA43 green resin.

## 3. Experimental procedures

All pitches and resins were ground to particle sizes of  $< 600 \mu\text{m}$ . They were carbonized individually in a 'Carbolite' horizontal electrical tube furnace to a heat treatment temperature (HTT) of 1173 K (900°C) at  $3 \text{ K min}^{-1}$  under nitrogen.

Blends of A240 and D112 with each of the CS217 and SC1008 resins were carbonized in a 'Carbolite' horizontal electrical tube furnace to 1173 K (900°C) at  $3 \text{ K min}^{-1}$ , in weight ratios of 10/90, 20/80, 30/70, 40/60, 50/50 and 90/10 (A240 + resin) and 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 (D112 + resin). A240 pitch + CS217 resin was also carbonized in the ratio 45/55. All carbons formed were mounted in resin, polished and examined optically. The carbons showing optical textures intermediate between the texture of carbon from the pitch carbonized singly and isotropic optical texture of the resin carbon (45% A240 + 55% CS217, and 80% D112 + 20% CS217) were prepared under pressures of 0.45 and 1.0 MPa (70 and 150 psi) (A240 + resin) and 0.73 and 1.1 MPa (110 and 165 psi) (D112 + resin), the pressures being generated by volatile evolution. These pressure carbonizations were carried out in a stainless steel pressure vessel connected to a digital pressure transducer [5]. Carbons from these blends were also examined under the optical microscope.

Blends of A240 and Esso CP1510 with HA43 green resins were prepared in the weight ratios 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70 and 20/80.

Each of the 16 blends were carbonized at atmospheric pressure in a Carbolite horizontal electrical tube furnace to an HTT of 1173 K (900°C) at  $3 \text{ K min}^{-1}$  under nitrogen. The carbons formed were mounted in resin, polished and examined under the optical microscope.

Each of the 16 blends was also carbonized in sealed gold tubes at a pressure of 200 MPa (30 000 psi) in a hydraulically pressurized stainless steel pressure reaction vessel [5] to an HTT of 873 K (600°C) at  $5 \text{ K min}^{-1}$ , 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. Each carbon was mounted in resin, polished and examined under the optical microscope.

## 4. Results

Table I lists the nomenclature used to describe the optical texture of carbons. The descriptions of optical textures of carbons from co-carbonizations at atmospheric pressure and 200 MPa are in Tables II to VIII. Selected micrographs of optical texture are shown in Figs. 1 to 8.

### 4.1. Carbonizations of A240 and D112 with CS217 under pressure

A240 and CS217 (45/55) carbonized at 0.45 MPa (Fig. 1) formed a carbon with medium-grained mosaic optical texture (Position A) with some isotropic areas (Position B). The same blend carbonized at 1.0 MPa formed a carbon with uniform fine-grained mosaic texture.

D112 + CS217 (80/20) carbonized at 0.73 MPa (Fig. 2) formed a carbon with uniform medium-grained mosaic optical texture. The same blend carbonized at 1.1 MPa formed a carbon with fine-grained mosaic texture.

TABLE I Nomenclature: optical texture in cokes

Isotropic	I	No optical activity
Very fine-grained mosaics	VMf	$< 0.5 \mu\text{m}$ diameter
Fine-grained mosaics	Mf	0.5 to 1.5 $\mu\text{m}$ diameter
Medium-grained mosaics	Mm	1.5 to 5.0 $\mu\text{m}$ diameter
Coarse-grained mosaics	Mc	5.0 to 10.0 $\mu\text{m}$ diameter
Supra-mosaics	SM	Aligned mosaics
Medium-flow anisotropy	MFA	$< 30 \mu\text{m}$ length; $< 5 \mu\text{m}$ width
Coarse-flow anisotropy	CFA	30 to 60 $\mu\text{m}$ length 5 to 10 $\mu\text{m}$ width
Flow domain anisotropy	FD	$> 60 \mu\text{m}$ length; $> 10 \mu\text{m}$ width
Small domains	SD	10 to 60 $\mu\text{m}$ diameter
Domains	D	$> 60 \mu\text{m}$ diameter

D<sub>b</sub>: basic, inherent anisotropy from coal.

D<sub>m</sub>: domains from mesophase.

TABLE II Optical texture of singly carbonized pitches and resins

Parent material	Description of optical texture	Percentage yield
A240 pitch	Flow domain anisotropy	35
D112 coal extract	Coarse-grained mosaics	32
Esso CP1510 pitch	Flow domain anisotropy	37
CS217	Isotropic	65
SC1008	Isotropic	40
HA43 green resin	Isotropic	85

## 4.2. Carbonizations of A240 and Esso CP1510 with HA43 resin

### 4.2.1. A240 + HA43: atmospheric pressure

For all the A240 + HA43 blends examined (ratios 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80) a two phase system resulted from the co-carbonizations. In each carbon, the interface between the flow domain anisotropy of the carbon from A240 pitch and the isotropic carbon from the resin was sharp and distinct with no apparent reaction having taken place between the pitch and resin (e.g. Fig. 3, pitch carbon, Position C, and resin carbon, Position D). The blend ratio had no effect upon the formation of this two phase system; in each blend the carbon from A240 acts as a binder holding the particles of resin carbon together. Particle size also has no apparent effect; small particles (with more surface area proportionally) did not react with the pitch (Fig. 3, Position D).

### 4.2.2. Esso CP1510 with HA43: atmospheric pressure

For all the Esso CP1510 + HA43 blends examined a two phase system resulted from the co-carbonizations. The interface between the flow domain anisotropy of the pitch carbon (Fig. 7, Position K) and the isotropic resin carbon (Pos-

TABLE III Carbonizations of A240 pitch with CS217 resin: atmospheric pressure

Ratio A240/CS217	Description of resultant optical texture	Percentage yield
20/80	Isotropic, with a few small (~ 1 μm) areas of anisotropy	36
30/70	Isotropic, with some small (~ 1 μm) areas of anisotropy	35
40/60	Fine-grained mosaic	33
45/55	Coarse-grained mosaic	32
50/50	Coarse-flow anisotropy	32
90/10	Flow domain anisotropy	41

TABLE IV Carbonizations of A240 pitch with SC1008 resin: atmospheric pressure

Ratio A240/SC1008	Description of resultant optical texture	Percentage yield
10/90	Isotropic with spheres of anisotropic material (~ 1 to 10 μm) near pore walls.	39
20/80	Isotropic with medium flow anisotropy near pore walls graduating into fine-grained mosaic before becoming isotropic	37
30/70	Equal areas of isotropic and coarse-grained mosaic with some large (~ 20 μm) spherical structures.	35
40/60	Some areas of isotropic areas of medium- and coarse-grained mosaic and medium flow anisotropy.	28
50/50	Coarse-flow anisotropy.	17
90/10	Flow domain anisotropy.	44

ition L) was sharp with no reaction having apparently occurred between the two.

## 5. Discussion

### 5.1. Carbonization of A240 and D112 with CS217 and SC1008 at atmospheric pressure and at high pressure (Tables II to VI)

#### 5.1.1. Atmospheric pressure

The above results and Tables II to VI indicate that the SC1008 resin is largely immiscible with the A240 pitch, forming a two phase system. It does produce some modifications in size of anisotropy with D112 but still forms a two phase system on carbonization. It therefore seems that this resin is unsuitable for use in producing a matrix of suitable optical texture for impregnation of carbon cloths, etc.

The CS217 resin produced a more uniform optical texture with both the A240 and D112. The resultant carbons were all single-phase materials. When carbonized with A240 pitch in different

TABLE V Carbonizations of D112 pitch with CS217 resin: atmospheric pressure

Ratio D112/CS217	Description of resultant optical texture	Percentage yield
60/40	Isotropic	42
70/30	Very fine-grained mosaic	42
80/20	Fine-grained mosaic	45
90/10	Medium-grained mosaic	46

TABLE VI Carbonizations of D112 pitch with SC1008 resin: atmospheric pressure

Ratio D112/SC1008	Description of resultant optical texture	Percentage yield
40/60	Isotropic with a few small areas (~ 1 μm) of anisotropy.	42
50/50	Equal amounts of isotropic and fine-grained mosaic, with clearly defined interfaces.	44
60/40	Small areas of isotropy with clearly defined interfaces. Mostly fine-grained mosaic.	45
70/30	Small areas of isotropy with clearly defined interfaces. Mostly fine-grained and medium-grained mosaics.	45
80/20	Small areas of isotropy with clearly defined interfaces. Mostly medium-grained mosaic.	45
90/10	Medium- and coarse-grained mosaics.	31

proportions the CS217 resin can be used to produce a range of uniform optical textures from fine-grained mosaic through to flow domain anisotropy. With D112 coal extract the range of optical texture produced is from very fine-grained mosaic through to medium-grained mosaic. This resin therefore seems to be a suitable additive to modify size of optical texture to give an optimum blend for impregnation of carbon cloths, etc. Size of optical texture may be varied by varying percentage additions of the resin.

TABLE VII Carbonizations of A240 pitch with HA43 resin: 200 MPa (30 000 psi) pressure

Ratio A240/HA43	Description of resultant optical texture
90/10 } 80/20 }	Predominantly coarse-grained mosaic (Fig. 4, Position E), with some small isotropic areas. Some botryoidal structures have formed (Position E).
70/30 } 60/40 }	
50/50 } 40/60 } 30/70 } 20/80 }	Some areas of small domain anisotropy (Fig. 5, Position G) with areas of isotropic resin carbon (Position H). The interface between the two carbons is not sharp but consists of a region up to 40 μm wide of fine-grained mosaic. A two phase system is formed with sharp interfaces between the coarse-grained mosaic anisotropy of the pitch carbon (Fig. 6, Position I) and the isotropic resin carbon (Position J).

TABLE VIII Carbonization of Esso CP1510 pitch with HA43 resin: 200 MPa pressure

Ratio Esso CP1510/HA43	Description of resultant optical texture
90/10 } 80/20 }	~ 50% botryoidal structures of coarse-grained mosaic texture (Fig. 8, Position M) and ~ 50% isotropic carbon (Position N). Both phases must have passed through a fluid phase as the pitch carbon has been penetrated by the fluid resin (the isotropic phase completely surrounds the botryoidal spheres).
70/30 } 60/40 }	
50/50 } 40/60 } 30/70 } 20/80 }	Areas of botryoidal structures of coarse-grained mosaic texture showing a sharp interface with areas of isotropic resin carbon. Areas of anisotropy showing sharp interfaces with areas of isotropic resin carbon. Size of optical texture decreases with amount of pitch in the blend from medium-grained mosaic (50/50) to fine-grained mosaic (20/80).

Yields on carbonization were not significantly increased for the A240 blends but yields on D112 blends were consistently ~ 10% higher than for the D112 single substance carbonizations. It therefore seems that addition of resin to some pitch carbonizations can improve carbonization yield.

### 5.1.2. Pressures in the range 0.45 to 1.1 MPa

The effect of carbonizing A240 + CS217 under a pressure of 0.45 MPa produced no significant change from the optical texture seen at atmospheric pressure; medium-grained mosaic. However,

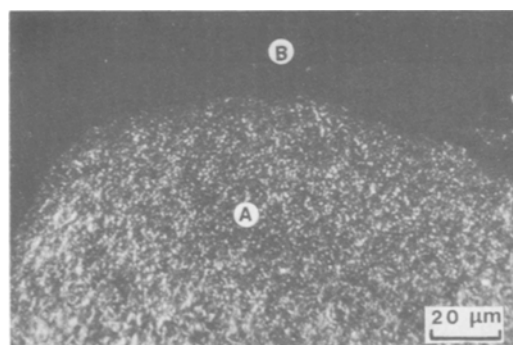
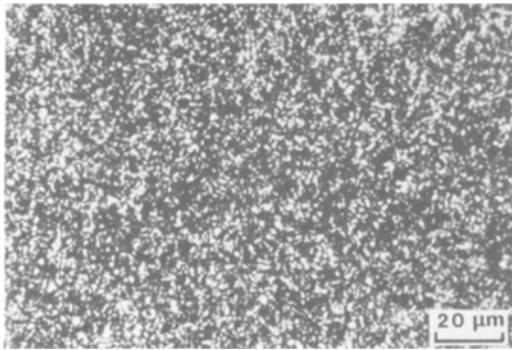
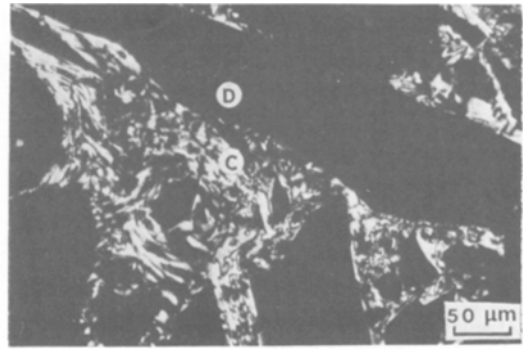


Figure 1 Optical texture of carbon from A240/CS217, 45/55, 0.45 MPa, showing medium-grained mosaics of pitch carbon (Position A) and isotropic resin carbon (Position B).



*Figure 2* Optical texture of carbon from D112/CS217, 80/20, 0.73 MPa, showing uniform medium-grained mosaics.



*Figure 3* Optical texture of carbon from A240/HA43, 80/20, atmospheric pressure, showing coarse-grained mosaics of pitch carbon (Position C) and isotropic resin carbon (Position D).

increasing carbonization pressure to 1.0 MPa reduced the size of the texture to fine-grained mosaic. With the D112 + CS217 blend, the effect of 0.73 MPa carbonization pressure was to *increase* the size of optical texture from that formed at atmospheric pressure. A further increase in pressure, to 1.1 MPa, reduced the size of optical texture of resultant carbons to fine-grained mosaic.

The initial increase in size of optical texture may be due to retention of organic material which would normally be lost as volatile matter within the carbonization system when carbonized under pressure. The subsequent decrease in size is consistent with results discussed previously [5], i.e. the hindrance of growth and coalescence of mesophase by pressure because pressure increases viscosity of mesophase.

## 5.2. Carbonization of A240 and Esso CP1510 with HA43 resin at atmospheric pressure and 200 MPa (Tables VII, VIII)

Co-carbonizations of HA43 resin with A240 and Esso CP1510 pitches under atmospheric pressure and at all the blend ratios used produced a two phase carbon system in which the resin and pitch did not interact.

At atmospheric pressure, therefore, A240 and Esso CP1510 pitches do not form a blend with HA43 resin suitable for impregnating composites.

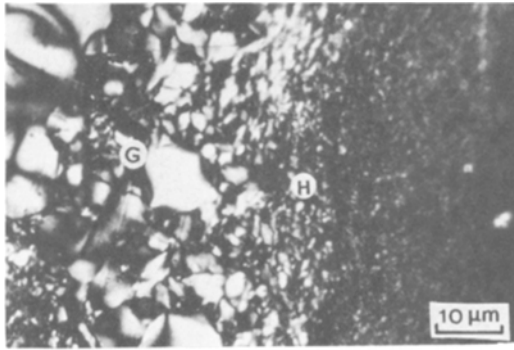
The results obtained with carbonization of these blends under high pressures, however, indicate that it may be possible to improve the interaction of blend components by this method. At least another type of matrix carbon may be prepared. A largely one phase system was obtained from A240 pitch when co-carbonized with small

amounts of the resin. This indicates that the resin has dissolved almost completely in the pitch when carbonized under pressure. With larger percentages of resin added there was less complete interaction of the resin and pitch but still more than for the carbonization under atmospheric pressure. The graded optical texture at interfaces of pitch carbon/resin carbon in the A240 + HA43 blends indicates that the resin, while not dissolving completely in the pitch, is reacting with it to produce areas of optical texture intermediate between that of the pitch carbon and that of the resin carbon.

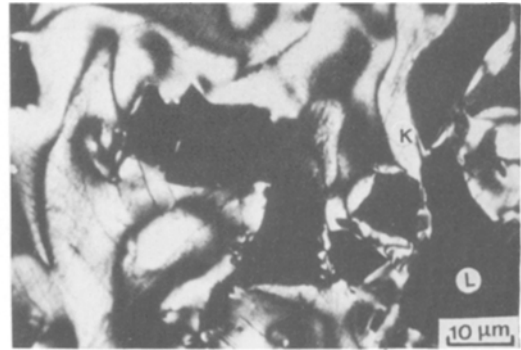
The modification of optical texture of the carbon from Esso CP1510 from coarse-grained mosaic to fine-grained mosaic with increase in percentage of resin addition indicates that the pitch has reacted with the resin. This reaction was not observed in atmospheric pressure carbonizations.



*Figure 4* Optical texture of carbon from A240/HA43, 90/10, 200 MPa, showing coarse-grained mosaics (Position E) and botryoidal structures (Position F).



*Figure 5* Optical texture of carbon from A240/HA43, 70/30, 200 MPa, showing small domain anisotropy of pitch carbon (Position G) separated by a diffuse interface from isotropic resin carbon (Position H).



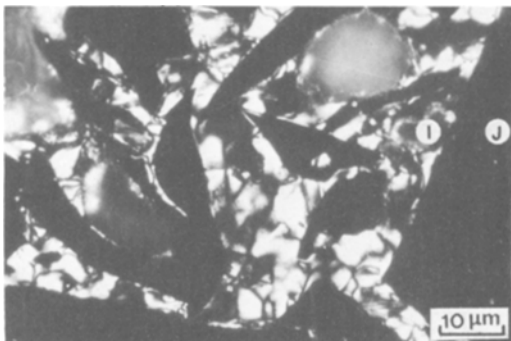
*Figure 7* Optical texture of carbon from Esso CP1510/HA43, 30/70, atmospheric pressure, showing flow domain anisotropy of pitch carbon (Position K) and isotropic carbon (Position L).

The results of the co-carbonization of Esso CP1510 + HA43 in the ratios 90:10 and 80:20 produced interesting results; two phases resulted, one is isotropic and one anisotropic but both having passed through a fluid phase and comprising ~ 50% each of the carbon structure. This seems to indicate that the resin reacted with slightly less than half of the pitch present (i.e. considerably more than its own weight in pitch) to produce a fluid phase which has apparently not gone through the liquid crystal phase change but has remained isotropic. The pitch which did not react with, or dissolve in, the resin, has produced botryoidal\* anisotropic structures typical of the parent pitch. It may be of interest to investigate further the behaviour of this type of matrix precursor when carbonized with fibres or fibre cloths. The mechan-

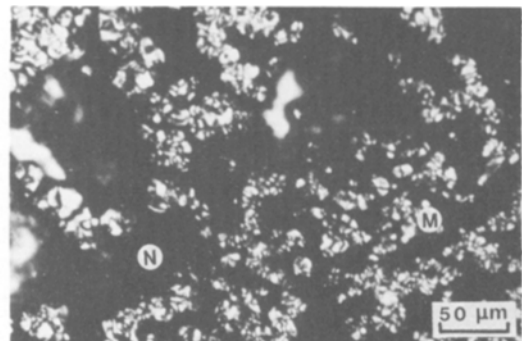
ical properties of this unusual type of structure may be relevant.

## 6. Conclusions

These results indicate that some commercially available high char-yielding resins may prove suitable for co-carbonization with pitches to produce matrix carbons of suitable high carbon yield and optical texture in carbon/carbon fibre composites. At present, the suitability of such blend components must be determined experimentally. Carbonization under pressure can be used to improve the compatibility of blend components, possibly due to the retention in the system of organic material normally lost as volatile matter.



*Figure 6* Optical texture of carbon from A240/HA43, 40/60, 200 MPa, showing coarse-grained mosaics of pitch carbon (Position I) and isotropic resin carbon (Position J).



*Figure 8* Optical texture of carbon from Esso CP1510/HA43, 90/10, 200 MPa, showing coarse-grained botryoidal pitch coke (Position M) and isotropic resin carbon, (Position N).

\*Botryoidal structures are partially coalesced spherical structures formed in carbon carbonized under pressure. These have been discussed previously [5].

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