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MODIFICATION OF COAL-TAR PITCH FOR USE AS A PRECURSOR FOR MATRIX CARBON IN CARBON-CARBON COMPOSITES

by

Sarah Frances Myram BSc. (Hons)

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ABSTRACT

Key words: Coal-tar pitch, matrix precursor, carbon-carbon composite, sparging.

In this work a series of pitches was prepared from two binder pitches, A and B, by sparging with hydrogen- and oxygen-containing gases, for different time intervals. The pitches were then characterised in terms of a number of chemical and physical properties. A model was developed which was used in conjunction with the pitch properties to determine whether sparging had involved chemical processes.

It was found that for pitch A, sparging with hydrogen- and oxygen-containing gases involved chemical changes but that these changes were independent of gas type. These chemical changes lead to an increase in toluene insoluble material. This material was unable to withstand pyrolysis and thus did not increase the carbon yield of the pitch. Since the reactions in pitch A were independent of gas type it was concluded that they were probably thermally induced.

For pitch B it was found that chemical reactions occurred and this time they were dependant on the gas type. The reactions that occurred for pitch B in hydrogen were concluded to be the same as those that occurred in pitch A but the reactions taking place in pitch B treated with oxygen were different. These reactions lead to an enhanced amount of toluene insoluble material. This material was able to withstand pyrolysis and hence increased the carbon yield. This reaction was predicted to be either an oxidative molecular growth or a decrease in volatility of polyaromatics brought about by the addition of oxygen functionality.

In the second stage of this work carbon composites were fabricated using the series of pitches as matrix precursors. The properties of the composites were obtained and examined to see if they correlated with the properties of the pitches used to make the composites. It was found that the composite characteristics correlated closely with their constituent pitch characteristics, especially in the fact that the characteristics of the composites made from pitches B treated with oxygen were markedly different from all the others. It was concluded that the characteristics that were notably different for pitches B treated with oxygen were a direct result of the different reactions that occurred in these pitches compared to the reactions that had occurred in the other pitches.
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1 INTRODUCTION

Composites are materials that are made from two or more distinct phases. The advantageous properties of each individual component is brought to the composite. Usually, a composite consists of a matrix and a reinforcement. The specific composite of interest in this work is the carbon-carbon composite which consists of a carbon reinforcement, that may be particulate or fibrous, embedded in a carbonaceous matrix that has been formed from an organic precursor. These composites have thermal properties that are superior to any other material. They have high thermal stabilities in inert atmospheres, high resistance to thermal shock due to high thermal conductivity and low thermal expansion behaviour. Carbon-carbon composites have high specific stiffness and strength at high temperatures of up to 2500°C [1]. No other materials compete in terms of their mechanical properties at such elevated temperatures. Other advantageous properties include low density, chemical inertness and biocompatibility.

These properties lead to many industry, military, aerospace and automotives applications [1]. Specific applications include brake discs for aerospace and advanced automotive systems, rocket nozzles, refractory tiles for fusion reactors and most recently, electrode components for advanced fuel systems.

The preparation of carbon-carbon composites involves the impregnation of carbon fibre cloth with a matrix precursor which is converted into carbon on subsequent heat treatment. Chemical vapour infiltration is the most commonly used method of impregnation but it involves high capital costs. Liquid phase impregnation, which involves lower capital costs, is the alternative. Impregnants that may be used are thermosetting resins or thermoplastic pitches. In this work coal tar pitch, which is a very cheap raw material, is the impregnant of interest.

Impregnation using a liquid impregnant such as coal tar pitch leads to low carbon yields, low densities and high porosities of the composite. Subsequently many impregnation and carbonisation stages are required to obtain the required carbon yields and densities. This leads to a costly and time consuming process.

Many pre-treatments of coal tar pitch are possible to improve the performance of the pitch as a matrix precursor. For example two pretreatments that are in use are
the extensive removal of volatiles by heat treatment [2] and the controlled condensation and addition of coking accelerators [3,4]. The method particularly relevant to this paper is the air blowing or ‘sparging’ of pitches. This method involves simultaneously heat treating molten pitches whilst blowing air or some gaseous mixture through the pitch.

There are contradictory reports in the literature that have been summarised by Menendez et. Al. [5] as to whether sparging involves chemical processes or whether it is simply a volatile stripping process. It is also not clear whether any chemical reactions that occur are dependent on the sparge gas. This project aims to resolve these two uncertainties.

In this project a series of pitches was prepared from two coal tar binder pitches, A and B, by sparging with hydrogen- and oxygen-containing gases for different time intervals. The pitches were then characterised in terms of a number of physical and chemical properties. A model was developed for the gas-sparging process and the experimental data was fitted to this model to determine whether chemical reactions were involved in the sparging, and whether any reactions occurring were different for the different pitches and different gases.

In the second half of this work, composites were fabricated using the different pitches as matrix precursors. The composite properties were also determined. The composite characteristics were compared to the pitch characteristics and it was found that a correlation existed.

This thesis is divided into 5 sections. Section 1 is the introduction. The relevant literature is reviewed in section 2. Experimental procedures are described in section 3. Section 4 presents the results and discussion, firstly for the pitch characteristics and secondly for the composite characteristics. The conclusions are presented in section 5 and section 6 is a set of recommendations for future work. References follow after section 6.
2 LITERATURE REVIEW

2.1 Carbon as a solid

2.1.1 The Element Carbon

Carbon has an atomic weight of 12.011 and is the sixth element in the periodic table. The properties of carbon depend on its electronic configuration which is \(1s^2 2s^2 2p^2\). However this ground state is almost unknown due to the energetic advantage of involving all of the four outer electrons in bonds with other carbon atoms or other atoms. The ability of carbon to form such stable bonds explains why there are millions of carbon compounds compared to perhaps a few dozen formed by most elements. The central chemicals of all living things are all carbon based and many carbon compounds, such as fuels and plastics, have become essential to our way of life. In the bonding of carbon the 2s-orbital and three 2p-orbitals are hybridised in one of three ways giving either two sp and two p orbitals or three \(sp^2\) and one p-orbital or four \(sp^3\) orbitals.

Carbon has three known isotopes \(^{12}\text{C}\), \(^{13}\text{C}\) and \(^{14}\text{C}\). Naturally occurring carbon consists of 98.90% \(^{12}\text{C}\) and 1.10% \(^{13}\text{C}\). Because of its large abundance and combining power \(^{12}\text{C}\) is defined as having an atomic mass of 12 exactly and all other atomic masses are defined relative to this [6]. \(^{13}\text{C}\) has a magnetic moment (spin = \(\frac{1}{2}\)) and so is used as a tool in NMR studies. \(^{14}\text{C}\) is a radioactive isotope and is formed by the interaction of neutrons with nitrogen in the upper atmosphere:

\[
N^{14} + n \rightarrow C^{14} + H^1
\]

Its half life is relatively long at 5730 years and hence the isotope finds application in dating archaeological remains and as a label when studying reaction mechanisms.
2.1.2 Allotropes of Carbon

Carbon exists in two known allotropic forms, diamond and graphite. At ambient pressures and temperatures graphite is the most thermally stable allotrope:

$$C_{(diamond)} \rightarrow C_{(graphite)} \quad \Delta H = -2.1 \text{ kJ mol}^{-1}$$

However, in terms of kinetics the change is extremely slow at room temperature due to a high activation energy resulting from the large number of bonds that must be rearranged.

In graphite, the 2s-orbital and three 2p-orbitals of each carbon atom are hybridised to three $sp^2$ orbitals and one $p$-orbital. The three $sp^2$ orbitals overlap with $sp^2$ orbitals on other carbon atoms to form three $\sigma$-bonds with bonding angles of 120° and layers of hexagonal two-dimensional assemblies result. The $p$-orbital from each carbon overlaps with the $p$-orbital from an adjacent carbon atom to form a $\pi$-bond. In actual fact, the electrons involved in $\pi$-bonds are delocalised over the assemblies. These assemblies are held loosely together by Van der Waals forces. In natural graphites the stacking of the layers is mainly hexagonal (ABAB) (figure 1a) and a small proportion is rhombohedral (ABCABC) (figure 1b).

Figure 1. The structure of graphite: (a) Hexagonal (ABAB) stacking, (b) Rhombohedral (ABCABC) stacking
In diamond, the 2s-orbital and three 2p-orbitals of each carbon atom are hybridised to form four sp\textsuperscript{3} orbitals. All four sp\textsuperscript{3} orbitals overlap with sp\textsuperscript{3} orbitals on other carbon atoms to form four σ-bonds. A very stable three dimensional tetrahedral structure results (figure 2). This structure is very rigid and the bonds are very strong and as a result, diamond is the hardest known material.

![Figure 2. The structure of diamond](image)

For a long time it was thought that diamond and graphite were the only existing allotropes of carbon but in 1985 Sir Harold W. Kroto discovered that in the plasma produced by a laser focused on a graphite target a third quite incredible form of pure carbon, Carbon 60, was present [7]. Carbon-60 was being formed by the gas phase nucleation of the carbon from the vaporised graphite. This form of carbon was found to be very stable and the structure proposed and later confirmed to explain this stability was a cage structure consisting of 12 pentagons and 20 hexagons with the symmetry of a soccer ball (figure 3)[8].
All the carbons in \( C_{60} \) are equivalent. They are \( sp^2 \) hybridised and each one belongs simultaneously to one five-membered ring and two six-membered rings. The strain caused by the distortion of the rings from coplanarity is equally distributed among all the carbons. The ball-like structure of carbon-60 was compared to the geodesic domes invented by the American architect, R. Buckminster Fuller and were hence named as buckminsterfullerene or bucky-balls for short. The term fullerene is now used for spherical carbon clusters of which there are many. For example another fullerene is \( C_{70} \) which has an elongated soccer-ball structure in which all carbons are not equivalent (figure 4)[8].
Since the discovery of C₆₀ it has been widely researched especially since it was found in 1990 [9] that it could be prepared in amounts sufficient for its isolation, purification and detailed study.

2.2 Synthetic Carbons

2.2.1 Formation of synthetic carbons

Solid synthetic carbons are produced from mainly organic precursors by the process of carbonisation. Carbonisation is defined [10] as a process of formation of material with increasing carbon content from organic material, usually by pyrolysis, ending up with an almost pure carbon residue at temperatures up to 1600K. The structure of such carbons is based on graphite but they have incomplete graphite structures. There are, in general, two types of carbon: firstly the isotropic, non graphitising type and secondly the anisotropic, graphitising form. Graphitisation is defined [10] as a solid state transformation of thermodynamically unstable non graphitic carbon into graphite by thermal activation.

Franklin [11] proposed models of graphitising and non graphitising carbon which have stood the test of time (figure 5)

Figure 5. Models of graphitising and non-graphitising carbon structures [11]
Isotropic carbons have graphitic layers that are small in size and which are bent, twisted and imperfect leading to random orientation with little parallel stacking over small areas. In anisotropic carbons the graphite layers are larger than those in isotropic carbons and have fewer structural defects with more parallel stacking which will increase on heat treatment to give a graphitic structure (graphitisation). The degree of isotropy and anisotropy of a carbon material will seem to vary depending on the method used to assess it. For example, a carbon may seem isotropic to the resolution of optical microscopy of ~0.5 μm but under the resolution of an electron microscope of nanometers, the carbon may show anisotropy. There is no clear boundary between an isotropic carbon and an anisotropic one but instead a gradation from one type to the other. On one end of the scale is the most isotropic carbon but this will still have some graphitic domains and on the other end of the scale is the best graphite but this will have some defects.

2.2.2 Non-graphitising carbons

Non-graphitising carbons are the first main category of synthetic carbons. They also have a large amount of associated literature and their properties are summarised well in the review of Jenkins and Kawamura [12]. Non-graphitising carbons are also known as amorphous or polymeric carbons. As the latter name suggests, they are formed from polymeric precursors. Some examples of non graphitising carbon precursors are cellulose from wood, nuts, nut shells, and non fusing coals such as lignites and anthracites and most polymeric biomass materials as well as the synthetic resins: phenolic resin, polyfurfuryl alcohol, polyacrylonitrile and polyvinylidene chloride.

In general, non graphitising carbons are formed from parent materials that do not pass through a fluid state on pyrolysis i.e. from thermosetting precursors. The material produced by carbonisation is a hard material known as a char. If the precursor is isotropic then the char will be isotropic and similarly if the precursor is anisotropic then the char will be anisotropic. In both cases the material is not graphitised even when heated up to 2700°C. The only way graphitic microstructure is obtained from thermosetting precursors is by applied or induced stress (such as...
shrinkage stress) during heat treatment or by the introduction of a catalyst, for example, adding Ni to a phenolic produces small domains of highly graphitic structures [12].

2.2.3 Pyrolysis of thermosetting precursors

In general the pyrolysis of polymers is a process by which the polymeric chains remain intact and coalesce with neighbouring chains. Four main stages occur during pyrolysis [12]:

1) Pre-carbonisation

At the beginning of a rapid weight loss regime, loose molecules including remaining monomers and solvent molecules are removed and the material turns black.

2) Carbonisation

Carbonisation occurs at much lower temperatures for thermosetting materials than for thermoplastic ones. Carbonisation can begin at temperatures as low as 250°C. Between 300-500°C there is a rapid weight loss. Oxygen, nitrogen and chlorine etc. are removed at this stage. The time taken for the removal of non-carbon elements depends on the temperature and is in the order of minutes. During this stage much cross linking occurs before the melting point of the precursor is reached so that fusion cannot take place and the liquid state required for mesophase formation is not reached. At the end of this stage the ratio of C:H is still 2:1 as is typical of an aromatic ladder polymer.

3) Dehydrogenation

Between 500-1200°C the hydrogen is eliminated and the remaining C:H ratio depends on the heat treatment temperature. As dehydrogenation occurs the conductivity,
density, hardness and stiffness all increase and the damping and permeability
decrease.

(4) Annealing

At temperatures above 1200°C the component crystallites achieve greater perfection
and defects are removed. The material becomes slightly softer but remains relatively
hard and amorphous with respect to graphitisable materials even at temperatures
above 3000°C.

The initial and most important chemical reactions that occur during pyrolysis are:
(i) Bond cleavage at the most reactive molecular site to produce a free radical
intermediate.
(ii) Rearrangement of radicals to more stable intermediates.
(iii) Polymerisation of radical units.
(iv) Elimination of hydrogen to form polymerised structures.

The structure that results from an isotropic thermosetting precursor is an isotropic,
three-dimensional network of stacks of graphene layers like tangled ribbons. There
are three types of bonding present:

(1) Between closely spaced parallel ribbons exist Van der Waals forces which are
negligible compared with the other bonds
(2) There are C-C bonds within the ribbons. These are the stiffest type of bonds but
only result in a stiff macroscopic structure when there are highly oriented regions
within the ribbons, for example in carbon fibres.
(3) There are C-C bonds between the ribbons which prevent shear movement of layers
past each other and rotating of ribbons. This lack of motion caused by these bonds
account for values of Young’s modulus, hardness and strength that are higher than
expected for such an isotropic material.

10
The hardness and high strength of these materials suggests a degree of tetrahedral sp$^3$ cross links between the hexagonal layers.

### 2.2.4 Graphitising carbons

The second category of synthetic carbons are graphitising materials which are formed from parent materials that pass through a liquid, or plastic phase during pyrolysis. The material that results is known as a coke. The coke is anisotropic and will begin to graphitise when heated and will attain a distinct graphite structure at around 2000°C or above. Some examples of precursors that form graphitisable carbons are organics such as polyvinylchloride, coal tar pitch, petroleum pitch and fuseable coals.

### 2.2.5 Graphitisation of graphitising carbons

At temperatures up to 2500°C a mosaic type structure may remain but within uniformly oriented areas the order increases until a complete graphite structure is formed. At the same time anisotropic shrinkage occurs leading to shrinkage cracks in some higher temperature cokes.

The changes in lamellar structure of a graphitising carbon with increasing heat treatment temperatures including the carbonisation and graphitisation stages have been summarised in a model by Griffiths and Marsh, figure 6 [14].

Figure 6. A schematic model of the changes in lamellar structure of a graphitising carbon with increasing heat treatment [14].
2.3 Coal-Tar Pitch

Coal-tar pitch is the material being used in this study as a matrix precursor for carbon-carbon composites and so the properties of coal tar pitch and its suitability for this purpose are discussed in the next section. The development from coal tar pitch of the mesophase and the resultant anisotropic coke are also discussed.

2.3.1 Origin of coal-tar pitch

When bituminous coal is carbonised at 900-1100°C to form coke, coal-tar is a by-product. Smaller amounts of coal tar are also produced as by-products when coal is carbonised at lower temperatures to form domestic smokeless fuel. Coal-tar pitch is the residue left from coal-tar after the heavy oil (creosote or anthracene fractions) have been removed [15].

2.3.2 Chemical properties of coal-tar pitch

Coal-tar pitch is a complex mixture of organic compounds with relatively low molecular weights. Its exact composition depends on the original coal source and the methods used in the removal of the low molecular weight fractions from the coal-tar. Around 2/3 of the species in coal-tar pitch are highly aromatic [16] (from NMR studies 90% of the carbon in coal tar pitch is in an aromatic environment). Most of the compounds contain 3-6 rings and have boiling points between 340 and 550°C. The elemental constitution of coal-tar pitch is thus mainly C and H with small amounts of N, O and S. The C/H ratio is an approximate indication of the degree of aromaticity in the pitch.
2.3.3 Physical properties of coal-tar pitch

In general coal-tar pitches are thennoplastic with low softening points and low melt viscosities. The thennoplastic nature of coal-tar pitch can be useful in the fabrication of composites as it allows good infiltration into carbon fibre cloth but is also a disadvantage during pyrolysis of the composite when it becomes very liquid and leads to bloating. The density of coal-tar pitches is around $1.3 \text{ g cm}^{-3}$.

Coal-tar pitch can be characterised by its solubility in solvents such as hexane, pentane, benzene, toluene, pyridine and quinoline but pitches may have similar solubilities in these solvents but still have different molecular weight distributions and rheological properties. Coal-tar pitch is usually described as having three fractions [16]. The first fraction is the "C" component or $\alpha$ resins which are insoluble in quinoline or pyridine and thus also known as the QI (quinoline insoluble) fraction. This fraction consists of high molecular weight aromatics ($M_R$~1500 or above) and solid impurities. The QI fraction is made up of primary particulates from the raw material that are completely insoluble in quinoline and the secondary particulates which are produced by the heat treatment of the pitch. The secondary particulates are small already developed mesophase units that are partly soluble and partly insoluble in quinoline. So the QI is not an absolute measure of particulate matter but is often used as a reference value of particulate inclusions.

The next fraction is the "C$_2$" component or $\beta$ resins which is soluble in quinoline or pyridine but insoluble in benzene or toluene and hence called the TI (toluene insoluble) fraction. This contains species of $M_R$ from 500-1500. The third fraction contains material that is soluble in benzene or toluene but insoluble in petroleum ether or n-hexane (or n-pentane). This is mainly the asphaltenes with $M_R$ between 300-460.
2.3.4 Pyrolysis of coal-tar pitch

On pyrolysis, coal-tar pitch which is isotropic in structure, passes through an intermediate liquid state called the "mesophase" and then solidifies to a highly orientated anisotropic semi-coke. Carbon yields after carbonisation at atmospheric pressure are around 50%. This is quite a high carbon yield compared to other materials that are used as matrix precursors but ideally it requires some improvement and if carbonisation takes place under nitrogen at a pressure of 10MPa it is possible to obtain carbon yields of around 90% [17]. (Pressures much higher than this have little additional effect). Slower rates of carbonisation also increases carbon yield. Pressure during pyrolysis also affects the microstructure of the coke. Low pressures form a needle like coke due to gas bubbles percolating through the structure. High pressures reduce these effects and a coarse, more isotropic coke is formed. Mesophase formation occurs at a lower temperature under a high pressure but very high pressures (~20MPa) prevent coalescence of spheres. When the carbonised pitch is then heated to temperatures above 2500°C it forms a high density (~2g cm$^{-3}$) graphitic structure.

2.3.5 Chemistry of pitch pyrolysis

Mesophase forming pitches consist mainly of polynuclear aromatic hydrocarbons and some oxygen and nitrogen containing compounds. According to Lewis [17] carbonisation is a process involving aromatic growth and polymerisation. The original pitch may be considered to contain two types of molecule: those that will form part of the mesophase (mainly small aromatics), called mesogens and those that will not. The molecules that will not form part of the mesophase may be small molecules that are volatilised off or may join to, or indeed be transformed into molecules that will form part of the mesophase. Indeed the first stage of carbonisation is the aromatisation of non-aromatics and volatilisation of smaller molecules. A large proportion of the aromatics contained in the original pitch take part in the formation of mesophase. In general, a small aromatic structure is polymerised to an aromatic polymer which grows to a three dimensional polymeric, aromatic, graphitic structure.
After around 30% conversion of pitch to mesophase the mesophase spheres were found to be essentially insoluble in solvents [18]

2.3.6 Physical changes during pyrolysis: transformation diagram

Whitehouse and Rand [19] introduced a useful way of representing the pitch-mesophase-coke transformation. This model is shown in figure 7 [14].

![Two-dimensional transformation diagram](image)

**Figure 7. Two-dimensional transformation diagram**

Essentially it is a two dimensional plot of some average compositional characteristic such as H/C ratio or volatile content versus temperature. This model has been developed into a three dimensional model with a third axis for viscosity by Turpin [20]. The three dimensional model is shown in figure 8.
The three dimensional model, defines a surface within a space that has viscosity of the pitch on one axis, residual volatiles in the pitch on the second and temperature on the third. Each point on the surface defines a pitch characterised by a certain viscosity and amount of residual volatiles at a certain temperature. In general, as temperature increases, the viscosity of the pitch decreases as the pitch softens and becomes more plastic and liquid-like. Also as temperature increases the amount of residual volatiles decreases. These two trends define the basic shape of the surface.

The surface has two boundary lines. The first boundary is the decomposition line defined by a series of decomposition temperatures, $T_o$. At this boundary every pitch reaches its maximum temperature and decomposes by evolution of volatiles. A pitch containing more residual volatiles will have a lower temperature of decomposition than one with fewer residual volatiles. As the temperature of
decomposition of the pitch increases the amount of residual volatiles in a pitch decreases and its viscosity increases hence the decomposition line tends towards the top back corner of the cuboid space.

The second boundary is the glass transition line defined by a series of glass transition temperatures, $T_g$. At this boundary every pitch undergoes the transformation from a plastic state to a solid, glassy pitch. The model ends at this boundary because glassy pitches cannot be processed and are hence of little interest. The $T_g$ line is on a surface of constant viscosity corresponding to the pitch glassifying. Pitches with higher amounts of residual volatiles will have lower glass transition temperatures. The opposite is also true i.e. if the pitch contains fewer residual volatiles the pitch is still plastic at a higher temperature. Most pitches are glassy solids at room temperature.

The two boundary lines, $T_g$ and $T_o$, meet at a temperature where viscosity is about $10^{13}$ Pa s and residual volatiles are tending towards zero where the pitch will simultaneously undergo the glass transition and decompose.

Consider point A on the diagram which describes a pitch A with a certain amount of residual volatiles and a certain viscosity at temperature $T_A$. On increasing the temperature, the pitch will follow the line AB which describes decreasing viscosity at a constant value of residual volatiles to point B. At point B the amount of residual volatiles begins to decrease along the decomposition line. On increasing the temperature to point C and then begin to decrease the temperature the pitch does not follow the same path that it followed during increasing temperature because the pitch has been irreversibly transformed. It now follows the line CD until it reaches the glass transition curve and the pitch, now pitch D undergoes the glass transition at temperature $T_D$. The temperature at which the pitch D is now transformed to a glassy solid, $T_D$, is higher than $T_A$, the temperature at which the original pitch A is transformed into a glass.

The surface boundaries and surface itself cannot be defined exactly because the characteristics of each pitch at a given temperature depends on the dwell time at that temperature and the dwell times at all previous temperatures. For example a long dwell time at a given temperature will cause decrease in residual volatiles and increases in viscosity without the need for any further increase in temperature.
2.3.7 Development of mesophase in coal-tar pitch

It was previously observed [22] that isotropic thermoplastic organic precursors are pyrolysed into anisotropic semi-cokes. The intermediate stages in this transformation were first observed by Taylor in 1961 [28]. Taylor observed anisotropic spherical bodies forming and growing in the plastic carbonaceous material. They grew at the expense of the isotropic material until they formed a three dimensional mosaic intermediate structure called the mesophase. Since then many review articles have been published on the formation of anisotropic carbons from the liquid phase via the mesophase [18, 23-27].

The general pattern of behaviour in forming anisotropic carbons is as follows [18]: On heating the substance melts to an isotropic material of plastic or liquid consistency. As the temperature increases to between 350-500°C, small spheres or "spherulites", which are anisotropic under the microscope, appear (figure 9).

Figure 9. Spheres at an intermediate stage of development. Nearly all the spheres have circular outlines. (Reflected polarised light).
They may first be detected when they are 0.1μm in diameter but probably exist smaller than this. With further temperature increase the spheres increase in size. Size will also increase to a certain extent with time at a fixed temperature. At a certain stage the spheres become so large that they begin to interfere with each other and coalesce to form a “mosaic”. At a certain point there is a phase inversion of the material from an isotropic pitch containing mesosphere spherulites to a material where mesophase is the dominant phase and isotropic pitch spherulites are contained within the mesophase. When anisotropic material has completely replaced the plastic pitch like material then the transformation has occurred and now or shortly after, the anisotropic “mesophase” solidifies to semi-coke. (NB the term mesophase is applied to the substance from the time the spheres develop until the solidification.)

2.3.8 Structure of the spheres

The outline of the spheres is near perfect as in figure 9. Sphericity is impeded when the local proportion of spheres to pitch becomes as large as say 1:1 and the spheres interfere with each other (figure 10).

Figure 10. Spheres at a later stage than figure 9. The bodies have become distorted through mutual interference.
Another thing that impedes a perfectly spherical growth is the presence of solid particles in the pitch (figure 11).

![Image of mesophase sphere distortion](image)

**Figure 11. Distortion of a mesophase sphere by insoluble inclusions.**

However in general the bodies are spherical at intermediate stages of their growth. If, however, the mixture is stirred then cooled a more complex structure results. The pitch and mesophase are intimately mixed showing that both behave as liquids and mesophase may enclose droplets of pitch which may, in turn, enclose smaller droplets of mesophase.

Electron diffraction patterns of the spheres show a considerable degree of order. The structure of the spheres is deduced from these diffraction patterns to be lamellar as shown in figure 12.
Figure 12. Structure of a mesophase sphere (sectioned parallel to the main axis of symmetry)

Electron diffraction patterns of the spheres both after the sample has been cooled and at the temperature at which the spheres were formed are the same indicating that cooling the mesophase does not affect the structure. The spheres are in fact somewhere between a crystalline and a liquid phase and are generally considered to be a discotic nematic liquid crystalline phase. There is now comprehensive literature on this phase for example the book by Chadrasekhar [29]. The term liquid crystal signifies a state that is intermediate between a crystalline solid and an amorphous liquid. The spheres are generally said to be in a liquid crystalline phase but this is not strictly correct as the spheres do not go on to form a liquid phase. A discotic liquid crystal is made up of disc shaped molecules. There are two distinct categories of discotic liquid crystals: columnar and nematic. The columnar phase in its simplest form consists of discs stacked on top of each other aperiodically to form liquid-like columns. The nematic phase has an arrangement of discs with orientational order but no long range translational order.

2.3.9 Nucleation of the spheres

Solid surfaces are preferred sites for nucleation of mesophase growth and the larger the specific surface area of the solid, the greater their effect. Under the same conditions, pitches containing solid particles contain more and smaller spheres than
ones with no insoluble particles but both pitches contained the same proportion of mesophase.

There is a marked association between insoluble particles in pitch and the spheres. In pitches containing insoluble particles, in the early stages of sphere development, spheres only developed adjacent to the insoluble particles. The particles are not incorporated into the spheres but aggregate around the surface giving it an irregular shape (figure 11).

2.3.10 Growth of the spheres

Pitch mesophase is often considered to be a lyotropic liquid crystalline phase. At the beginning of the carbonisation of the pitch the concentration of mesogens increases due to non mesogens being volatilised or polymerising to form mesogens. At some critical concentration the mesogens start to precipitate out as mesophase. Increasing both temperature or time at a fixed temperature causes spheres to grow but there is a limiting temperature below which no spheres develop even after 24 hours and the increase in sphere growth at a fixed temperature appears to be asymptotic with time. The slower the rate of carbonisation, the fewer and larger the spheres are. At higher temperatures complete conversion to mesophase occurs and the higher the temperature the quicker the conversion is complete. Both stirring and the presence of fine particles accelerates the formation of mesophase.

2.3.11 Coalescence of the spheres.

As the spheres grow they begin to interfere with each other and coalesce. This occurs as in figure 13.
Figure 13. Rearrangement of lamellae when two spheres coalesce

As the spheres touch, their surfaces rearrange so that a continuous link is formed but at the other edges of the two spheres the lamellar arrangement is preserved. Eventually the composite contracts to form a complex sphere as in figure 14.

Figure 14. Small sphere (arrowed) and part of a large sphere showing complex internal structure (reflected polarised light)
This takes considerable time since the mesophase is highly viscous in most cases. When more than two spheres begin to coalesce a larger sphere does not always develop from them and coalescence of many spheres occurs in three dimensions. Eventually the mesophase contains areas of uniform orientation connected by zones where the lamellae curve sharply to conform to the orientation of the next uniform area. Hence even though the term mosaic is used, the boundaries of the uniform units are not sharply bounded.

After complete conversion to mesophase the material is still very viscous and holding in this liquid condition for a long period can result in regions of up to 1mm of constant orientation. If the temperature is now raised slightly the mesophase is converted into a semi-coke, probably a result of a gradual increase in viscosity. This series of events takes place at closer intervals of temperature for some materials than for others.

If the pitch contains insoluble particles, these are not incorporated into the mesophase but remain at the edges of where spheres coalesce forming a three dimensional network throughout the mesophase. The particulate matter hinders the coalescence of spheres and a smaller optical texture results. The network of particulates and the smaller optical texture that forms as a result of the particulates both affect the physical properties of the coke.
2.4 Matrix Materials for Carbon-Carbon Composites

According to Fitzer [30] a suitable matrix precursor for carbon-carbon composites must have the following properties:

1. High carbon yield even when carbonised at atmospheric pressure
2. Good fluidity and efficient wetting of the carbon substrate
3. Ability to produce matrices with low porosity, high density, high strength, good graphitisability and resistance to oxidation at high temperatures

There are two categories of material that are used as matrix precursors for carbon-carbon composites: thermoplastic precursors and thermosetting precursors.

2.4.1 The use of thermoplastic precursors in carbon-carbon composites

It has been found that pitches, derived from coal tar or petroleum are acceptable matrix precursors for carbon-carbon composites. The advantages of pitch are that it is inexpensive, it has excellent graphitisability and has the flexibility to produce composites of differing properties depending on the composite manufacture conditions. Some disadvantages of commercial pitches are that they have only moderate carbon yields and they develop quite a high porosity after carbonisation leading to poor physical and mechanical properties. Several impregnation and carbonisation cycles are required to improve these characteristics and this increases the price of the final product.

2.4.2 Pre-treatments of pitches for use as matrix precursors in carbon-carbon composites

It is possible to improve the density, decrease the porosity, and improve the carbon yield of pitch by various pre-treatments. The aim of any pre-treatment is to promote polymerisation of the pitch and decrease the content of volatile molecules. The reduced volatile content reduces the bloating effect caused by release of volatiles.
Procedures that have previously been used include the extensive removal of volatiles by heat treatment [2] and the controlled condensation and addition of coking accelerators [3,4]. The method particularly relevant to this paper is the air blowing or ‘sparging’ of pitches. This method involves simultaneously heat treating molten pitches whilst blowing air or some gasesous mixture through the pitch. In 1994 properties of pitches treated in this way were stated [31] and a set of reactions involving the oxidation of aromatic compounds were proposed to explain the properties. In 1995 Menendez et. Al. [5] performed air blowing on two types of pitch at three different temperatures: 250°C, 275°C and 300°C. The parent pitches were also heated under nitrogen at temperatures of 400°C, 425°C and 430°C to determine the effect of the heat treatment alone. The heat treated pitches were characterised and cokes produced by carbonising the pitches were also characterised. Finally, unidirectional carbon-carbon composites were made using the pitches and various tests were performed on these.

The main effects of the air blowing on the pitch were that their softening point increased, their carbon yield increased and the TI and Q1 fractions increased. No mesophase had developed during the air blowing at the temperatures used as the pitches were still totally isotropic. The C/H ratio clearly increased but the N, S and O contents were not significantly affected. There was a decrease in the number of aliphatic compounds.

In the series of thermally treated pitches, the softening point and carbon yield increased with temperature due to volatile release and polymerisation. Solubilities in hexane, benzene and pyridine all changed substantially during thermal treatment. Useful information about the structure of pitch matrix carbons can be obtained by studying the cokes made from carbonising the pitches even though the structure of the matrices are influenced by the presence of fibre and the carbonisation conditions used to make the composite. Menendez et. Al. [5] produced cokes from the pitches and these were themselves characterised. The cokes made from the air blown pitches had an increased amount of mosaics and a decreased contribution from domains (with decrease in size of domains). The formation of mesophase was, on the other hand, delayed with the air-blown pitches. The presence of fewer volatiles in the pitches prevented swelling during carbonisation and thus restricted the development of coke
porosity and reduced the amount of debonding and intra-matrix cracks to almost none.

Thermal treatment of the pitches alone led to no significant changes in the optical texture of the cokes. Porosity of cokes decreased slightly with the first two temperature treatments and decreased significantly at the highest heat treatment temperature.

The composites then made from the air blown pitches exhibited higher flexural strength and the failure mode went from pseudoplastic to brittle. The composites made using air blown pitches exhibited an increased interlaminar shear strength. These changes in mechanical properties were deduced to be a consequence of stronger matrix-fibre bonding and the decreased number of cracks and may also be due to improved matrix microstructure. The microstructure of the cokes from the air blown pitches had a larger contribution of mosaics than of domains. There were virtually no interfacial or intra-matrix cracks. The porosities of the composites were all very similar so the changes observed in the cokes were minimised in the composites due to the presence of fibre and operating conditions. The bulk density increased except at the higher air blowing temperatures when it decreased slightly.

The composites from thermally treated pitches did not show significant changes in optical texture compared with composites from the untreated pitch. As for air blowing, the thermal treatment led to most of the interface and intra-matrix cracks disappearing. Thermal treatment caused considerable improvement in composite strength and increased temperature of thermal treatment increased strength except at the highest temperature, 430°C, when the strength decreased. The increased strength could be, as for the air blowing treatment, due to virtually no interfacial or intra-matrix cracks and a stronger fibre matrix bonding.

2.4.3 The use of thermosetting matrix precursors in carbon-carbon composites

There are three requirements for thermosetting precursor suitability for use as matrix precursor in carbon-carbon composites:
(1) The carbonisation shrinkage of the matrix should not damage the carbon fibre skeleton

(2) The porosity formed during pyrolysis must be open and accessible to further impregnation

(3) The $T_g$ should ideally be above (or not much below) the decomposition / carbonisation temperature, otherwise the material will carbonise in a rubbery state.

The first advantage of using thermosetting matrix precursors for carbon-carbon composites is that such materials have historically been used as matrices in other composite materials and there are many established technologies for producing composites from them. Secondly, these materials have relatively high carbon yields. However the carbon yield can not be increased by the application of pressure during pyrolysis as is the case for thermoplastic materials. Table 1 [1] gives the carbon yields of various thermosetting precursors.

Table 1. Carbon yields of various thermosetting precursors

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Carbon Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic resins</td>
<td>50-55</td>
</tr>
<tr>
<td>Furan resins</td>
<td>50-60</td>
</tr>
<tr>
<td>Oxidised polystyrene</td>
<td>55</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>50</td>
</tr>
<tr>
<td>Polyaclrylonitrile</td>
<td>44</td>
</tr>
<tr>
<td>Polystyrene chloride</td>
<td>25</td>
</tr>
<tr>
<td>Cellulose</td>
<td>20</td>
</tr>
<tr>
<td>Epoxy resins</td>
<td>5</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>5</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>5</td>
</tr>
</tbody>
</table>

A disadvantage of using thermosetting materials as matrix precursors is that they carbonise to give low density carbon (1.5-1.6 g cm$^{-3}$) and thus require many reimpregnation/recarbonisation steps. Secondly, impurities in the precursor polymers lead to defects in the carbon structure and the variability in impurities in the precursors leads to a variability in the amount of defects and thus the strength of the carbon is not controllable by process parameters.
There are two thermosetting resins that have the properties to have been exploited commercially. The first materials are phenolic resins which are usually used for the initial impregnation stage; the second type of material are furan resins (and resin/pitch mixtures) which are used for further densification cycles.

Phenolic resins are polymers consisting of phenolic groups interspersed with methylene bridges. They are formed from the condensation of, for example, phenol and formaldehyde. Excess formaldehyde creates methylene bridges between the polymer chains. Furan Resins are made from furan which is derived from waste vegetable matter.
2.5 Strength of Carbon Materials

The strength of a solid material is defined as the maximum stress that the material can take before failure. If this stress continues to be applied then it will lead to fracture. The theoretical strength of a material is the stress required to break the bonds between two adjoining layers of atoms and depends on the distance between the layers. The theoretical stress is evaluated as:

\[ \sigma_{th} \approx 0.1E \]

where E is the elastic constant of the material.

In practice it is found that the strength of brittle materials is much lower at between 0.01E and 0.001E. This discrepancy for brittle solids, is well known to be due to the presence of small cracks which propagate and cause fracture below the theoretical strength of the material.

Since carbon fibres, coal tar pitch and carbon-carbon composites made using coal tar pitch are all brittle materials the theories and equations relating to brittle fracture are relevant to varying degrees and the obvious conclusion to draw is that it is favourable to reduce the number of flaws in such carbon materials in order to increase their strength.
2.5.1 Linear elastic fracture mechanics

The strength of solids is calculated using fracture mechanics. The original concepts of fracture mechanics applied only to materials that obey Hooke's Law i.e. linearly elastic materials which tend to be brittle solids such as the carbon materials of interest in this work. Theories have since been developed that account for various types of non-linear material and dynamic effects but all these theories are based on the original linear elastic fracture mechanics (LEFM). Section 2.5.2 first gives an atomic explanation fracture. Section 2.5.3 then describes the early work of Inglis who uses a stress intensity approach to describing fracture mechanics. Finally section 2.5.4 looks at the Griffith theory of brittle fracture which is used today to predict critical stresses of brittle materials.

2.5.2 Atomic view of fracture

Atoms are held together by attractive forces. To fracture a material it is necessary to apply sufficient stress to overcome the bond strength of the material. Figure 15 shows plots of potential energy and force versus atomic separation in a solid. To cause a fracture a tensile force must be applied to increase the atomic separation from its equilibrium value and this force must exceed the cohesive force between atoms to completely sever the bond and fracture the material.

The bond energy is given by

\[ E_b = \int_{x_0}^{\infty} F \, dx \]  

where \( x_0 \) is the equilibrium spacing and \( F \) is the applied force. This is equivalent to the fracture energy, \( E_F \).
We may idealise the relationship between force and displacement as one half of a sine wave

\[ F = F_c \sin \left( \frac{\pi x}{\lambda} \right) \]  

(2)

where \( \lambda \) is defined in figure 15 and \( F_c \) is the cohesive force

For small displacements from \( x_0 \), it can be approximated that the force displacement relationship is linear

\[ F = F_c \left( \frac{\pi x}{\lambda} \right) \]  

(3)

The elastic constant is then given by

\[ k = \frac{F_c \pi}{\lambda} \]  

(4)

Both sides of this equation are multiplied by the number of bonds per unit area, \( n / A \), and equilibrium spacing, \( x_0 \).

This converts \( k \) to Young's modulus, \( E \)

\[ \frac{k x_0}{A} = \frac{F_c x_0}{A} = \frac{F_c / A}{x / x_0} = E \]  

(5)

and \( F_c \) to cohesive stress, \( \sigma_c \):

\[ \frac{F_c x_0}{A} = \sigma_c x_0 \]  

(6)
thus equation (4) becomes

\[ E = \frac{\sigma \varepsilon x_0 \pi}{\lambda} \] (7)

Rearranging this equation for \( \sigma \varepsilon \) gives

\[ \sigma \varepsilon = \frac{EA}{\pi x_0} \] (8)

Assuming that \( \lambda \) is approximately equal to the equilibrium spacing, \( x_0 \) gives

\[ \sigma \varepsilon \approx \frac{E}{\pi} \] (9)

Substituting the unapproximated form of \( F \) from equation (2) into equation (1) allows a value of fracture energy to be calculated.

\[ E_f = \int_0^\frac{\lambda}{x} F \text{d}x = \int_0^\frac{\lambda}{x} F \sin \left( \frac{\pi x}{\lambda} \right) \text{d}x \] (10)

The fracture energy per unit surface area is

\[ E_f = \int_0^\frac{\lambda}{x} \sigma \varepsilon \sin \left( \frac{\pi x}{\lambda} \right) \text{d}x = 2 \sigma \varepsilon \frac{\lambda}{\pi} \] (11)

The surface energy per unit surface area, \( \gamma \), is equal to one half the fracture energy since two surfaces are created when a material fractures.

\[ \gamma = \frac{1}{2} \int_0^\frac{\lambda}{x} \sigma \varepsilon \sin \left( \frac{\pi x}{\lambda} \right) \text{d}x = \sigma \varepsilon \frac{\lambda}{\pi} \] (12)
Substituting equation (8) into equation (12) and solving for $\sigma_c$ gives an equation for the cohesive stress, that is, the stress required to overcome the cohesive forces in unit area of the material and hence cause it to fracture

$$\sigma_c = \sqrt{\frac{E\gamma}{x_o}} \quad (13)$$

This cohesive stress of a material is also known as the theoretical strength of a material, $\sigma_{th}$. In many materials the ratio $\sigma_{th} / E$ is in the range 0.1 to 0.2 $[33,34]$. In the case of graphite $\sigma_{th} = 0.1E$. However the strength of real materials is often much lower than $\sigma_{th}$, between 0.01E and 0.001E. This discrepancy is, as stated above, due to the presence of small cracks or flaws which propagate and cause fracture below the theoretical strength of the material. The next two sections derive relationships between flaws and strength of brittle materials.
Figure 15. Potential Energy and Force as a Function of Atomic Separation
2.5.3 Inglis theory of brittle fracture

The derivation in the previous section shows that the theoretical stress required for fracture or the "fracture strength" of a material is approximately $E / \pi$, but experimental fracture strengths are typically three to four orders of magnitude lower than this value. This discrepancy is due to flaws in the material. Fracture can only occur when the stress at atomic level exceeds the cohesive strength of the material. The presence of flaws must concentrate the local stress near the flaw thus allowing the material to fracture at the flaw when a global stress lower than the cohesive stress is applied. Inglis [34] provided the first evidence for stress concentration at flaws and his theory is presented here.

Consider an elliptical hole $2a$ long and $2b$ wide in a flat plate as in figure 16. Stress is applied to the plate perpendicular to the major axis of the ellipse. Assume that the plate boundaries do not affect the hole i.e. the plate width $\gg 2a$ and plate height $\gg 2b$.

![Diagram of elliptical hole in a flat plate](image)

Figure 16: Elliptical hole in a flat plate
It is found that the ratio of stress at the tip of the major axis (point A), $\sigma_A$, to the applied stress, $\sigma$, is given by

$$\frac{\sigma_A}{\sigma} = \left(1 + \frac{2a}{b}\right) \quad \text{(1)}$$

The ratio $\sigma_A / \sigma$ is defined as the stress concentration factor, $k_t$. When $a = b$ and the hole is circular, $k_t = 3$.

If we consider the stress at the crack tip we may replace $b$ in equation (1) by using the equation for the radius of curvature at the tip crack, $r$

$$r = \frac{b^2}{a} \quad \text{(2)}$$

Substituting for $b$ from (2) into (1) gives

$$\frac{\sigma_A}{\sigma} = \left(1 + 2\left(\frac{a}{r}\right)^{\frac{1}{2}}\right) \quad \text{(3)}$$

As the major axis, $a$, increases in length relative to $b$, the ellipse begins to become a sharp crack.

When $a >> b$ it follows from equation (2) that $a >> r$ and also $2\left(\frac{a}{r}\right)^{\frac{1}{2}} >> 1$ and thus equation (3) reduces to

$$\frac{\sigma_A}{\sigma} = 2\left(\frac{a}{r}\right)^{\frac{1}{2}} \quad \text{(4)}$$
So for narrow cracks i.e. ones with large a / b ratio the stress concentration factor at point A can take on values considerably larger than unity. The narrower the crack, the higher the stress concentration.

For an infinitely sharp crack where \( r = 0 \) this equation predicts an infinite stress at the crack tip. According to this theory a sharp crack should cause fracture in the material with an infinitesimal applied stress. This raises doubt in the theory since an infinitesimal applied stress could cause infinite stress and thus failure in a sharp crack but in practice an infinitesimal stress applied to a sharp crack will not cause failure. This doubt is what caused Griffith to develop a fracture theory based on energy considerations rather than local stress.

The idea of an infinitely sharp (and thus long) crack is not possible within a real material and the minimum radius of curvature a crack could have is on the order of the atomic radius i.e. \( r = \xi_0 \). Substituting \( r = \xi_0 \) into equation (4) gives the local stress concentration at the tip of an atomically sharp crack

\[
\frac{\sigma_A}{\sigma} = 2 \left( \frac{a}{\xi_0} \right)^{\frac{1}{2}} \tag{5}
\]

Now assume that a fracture occurs when the local stress concentration at point A is equal to the cohesive stress i.e. when \( \sigma_A = \sigma_c \). Equating equation (4) with equation (13) from the previous section results in the following expression for the remote fracture stress

\[
\sigma_f = \left( \frac{Ey}{4a} \right)^{\frac{1}{2}} \tag{6}
\]

Fracture stress varies inversely as the square root of the length of the crack. This suggests that fracture stress is decreased by the presence of flaws and that fracture stress is related to the shape and size of the flaw. It does not account for the effect of the size of the minor axis, \( b \), on the fracture stress.
2.5.4 Griffith theory of crack propagation

Griffith’s theory of crack propagation [35] is based on energy considerations rather than local stress. Griffith postulated that for a crack to propagate, two conditions apply:

1. It must be energetically desirable (total energy must decrease or remain constant)
2. There must be a molecular mechanism by which energy transformation can take place.

Consider an elastic body with a crack of length 2a. A stress, \( \sigma \), is applied to the outer boundary of the body as in figure 17 [36]. Assume that the plate width \( \gg 2a \) and that the stress causes plane stress in the body.

![Diagram of a through thickness crack in an infinitely wide plate subjected to a remote tensile stress](image)

Figure 17. A through thickness crack in an infinitely wide plate subjected to a remote tensile stress [36]
The total energy of the system, $U$, is given by:

$$U = (W + U_E) + U_s$$ (1)

where $W$ is the work done by the load, $U_E$ is the elastic strain energy stored in the body and $U_s$ is the surface free energy of the crack surfaces. The term in brackets is known as the mechanical energy.

At thermal equilibrium $W$ is zero so

$$\frac{dU}{da} = 0$$ (2)

or

$$-\frac{dU_E}{da} = \frac{dU_s}{da}$$ (3)

That is to say, if a crack is to propagate at thermal equilibrium with no external stress, the elastic strain energy must be enough to overcome the surface energy of the material.

For small displacements from equilibrium length, if $\frac{dU}{da}$ is negative the crack will extend reversibly and if it is positive the crack will close up reversibly.

From linear elasticity theory

$$W = 2U_E$$ (4)
From Inglis' stress analysis [34] the elastic strain energy of each volume element about the crack for unit width is given by

$$U_e = \frac{\pi a^2 \sigma^2}{E}$$  \hspace{1cm} (5)

The surface energy required for the creation of two crack surfaces of unit width is

$$U_s = 4\alpha \gamma$$  \hspace{1cm} (6)

where $\gamma$ is the free surface energy per unit area.

Combining equations (1) and (4) gives the following equation for the total energy of the system

$$U_s = (-2U_e + U_g) + U_s$$

$$= -U_e + U_s$$  \hspace{1cm} (7)

By substituting equations (5) and (6) into equation (7) the total energy of the system can be expressed as

$$U = -\frac{\pi a^2 \sigma^2}{E} + 4\alpha \gamma$$  \hspace{1cm} (8)
Figure 18 below is a graph of the total energy, $U = -U_E + U_S$, mechanical energy, $(-W + U_E) = -U_E$ and surface energy, $U_S$ versus the crack length (which is proportional to $a$).

Figure 18. Variation of the mechanical energy, $-U_E$, surface energy, $U_S$, and total energy, $U$, with crack length

The total energy of the system is maximum at $a_{critical}$. A crack of this length is unstable at the point of either extension, as increasing the crack length causes the total energy of the system to decrease, or at the point of closing up as decreasing the crack length also decreases the total energy of the system.
The maximum in total energy, $U$, occurs when

$$\frac{dU}{da} = 0 \quad (9)$$

which is also the equation for thermal equilibrium of the system.

Now

$$\frac{dU}{da} = \frac{d(-U_E)}{da} + \frac{dU_s}{da} \quad (10)$$

and so

$$\frac{d(-U_E)}{da} + \frac{dU_s}{da} = 0 \quad (11)$$

The derivative of elastic strain energy with respect to $a$ is

$$\frac{d(-U_E)}{da} = -\frac{2\pi a\sigma^2}{E} \quad (12)$$

and the derivative of surface energy with respect to $a$ is

$$\frac{dU_s}{da} = 4\gamma \quad (13)$$

Substituting equations (12) and (13) into (11) gives.

$$\frac{2\pi a\sigma^2}{E} = 4\gamma \quad (14)$$
This can be rearranged to give the Griffith equation for the stress needed to cause the theoretical crack to propagate and the material to fracture.

\[ \sigma_f = \left( \frac{2E \gamma}{\pi a} \right)^{\frac{1}{2}} \quad (15) \]

It can be seen that this critical stress is inversely proportional to the square root of the crack length. So the largest crack present in a body before application of stress determines its fracture stress. Unlike Inglis’ theory the value of symbol a in this equation can apply to the major or minor axis of the crack. Thus Griffith’s theory has fully incorporated the size of the crack in the critical fracture stress where Inglis’ theory only accounted for the size of the major axis, assuming that the major axis was much greater than the minor axis.
2.5.5 Comparison of Inglis and Griffith theories of fracture strength.

It is obvious that the two equations derived for the global fracture stress (equation (6) from Inglis theory and equation (15) from Griffith theory) are very similar and they do indeed differ by less than 40%. So in the case of a sharp crack in an ideally brittle solid, the two approaches are consistent with each other.

The two equations give diverging answers when the crack tip radius is significantly greater than the atomic spacing. The Griffith theory fracture stress is insensitive to the tip radius of curvature, \( r \). However this is after the assumption \( a \gg b \) has been made. The Inglis theory fracture stress (which incorporates that the stress attained at the crack tip must be of the order of \( \sigma_c \)) varies as \( \sqrt{r} \).

If we consider a crack with a tip radius of curvature of \( 5 \times 10^{-6} \) m (four orders of magnitude greater than the atomic spacing in a typical crystalline solid) then the Griffith fracture stress is going to be 100 times larger than Inglis’ fracture stress.

The behaviour of a real material is in fact somewhere between these extremes.

2.5.6 Modified Griffith equation

Equation (15) from the Griffith theory for fracture stress is only valid for ideally brittle solids. There is good agreement between Griffith’s equation and experimental fracture strengths of glass but the equation severely underestimates the fracture strength of metals. Irwin [37] and Orowan [38] independently modified the Griffith expression to include materials that exhibit plasticity.

The revised expression is

\[
\sigma_f = \left( \frac{2E(\gamma + \gamma_p)}{\pi a} \right)^{\frac{1}{2}}
\]

The plastic work done per unit area of surface created and is typically much larger than \( \gamma \) hence giving much larger fracture strengths in materials exhibiting some plastic behaviour. In a metal, when a bond breaks dislocation motion results in
additional energy dissipation whereas in an ideally brittle solid a crack is formed by just breaking bonds and the surface energy created, \( \gamma \), reflects the total energy of bonds broken per unit area.

The above equation (1) originally derived for metals can be generalised to account for any type of energy dissipation:

\[
\sigma_r = \left( \frac{2Ew_f}{\pi a} \right)^{\frac{1}{2}}
\]  

(2)

where \( w_f \) is the fracture energy which could include plastic, viscoelastic or viscoplastic effects depending on the material.

The fracture energy can also be influenced by crack meandering and branching which increase surface area. However it must be remembered that the Griffith model only applies to linear elastic material so any non-linear effects such as those described above must be confined to small regions near the crack tip and the global behaviour must be elastic. Also, the equation above assumes that \( w_f \) is constant which may not be the case as fracture energy increases with crack growth.
2.6 Carbon Fibres

2.6.1 Introduction to fibres as engineering materials

It is clear that the presence of flaws in a material limit the strength of the material and flaws lying perpendicular to an applied load are most significant in limiting strength. It follows, then, that fibres have high strengths parallel to their axis because flaws lying perpendicular to this direction are minimised. The strength of a fibre may also be elevated due to perfection in the crystal structure i.e. a fibre has a highly aligned crystal structure. This alignment also produces increased values of stiffness in the fibre compared with the bulk material. However, the effect on strength and stiffness of a highly oriented fibre is not as great as the increase in strength due to the minimising of flaws.

Figure 19 gives values of specific tensile modulus of some fibres and bulk materials and figure 20 is a plot of specific tensile strength vs. specific tensile modulus of some materials in their bulk and fibre forms.

![Graph showing specific tensile modulus comparison](image)

Figure 19. Specific Young's Modulus of carbon fibres compared with that of conventional materials [39]
Figure 20. Specific tensile strength and modulus of carbon fibres compared with those of conventional materials [40]

NB. Specific values of strength and modulus (strength and modulus relative to density) are often used because many manufacturing applications such as use in aircraft manufacture require materials with improved strength and stiffness without proportional increase in density. These figures illustrate the higher tensile strengths and moduli in fibres compared to bulk materials.

A fibre has been defined [41] to be “any material in an elongated form such that the ratio of its minimum length to its maximum average transverse dimension is 10:1, its maximum cross-sectional area is $7.9 \times 10^{-5} \text{ in}^2$ (corresponding to a circular cross section of 0.010 in diameter), and its transverse dimension is no greater than 0.010 in.”

Within the term ‘fibre’, there are two categories: the continuous fibre or “filament” and the discontinuous fibre. The ultimate discontinuous fibre is the whisker which is defined [41] as “Any material which fits into the definition of a fibre and is a single crystal.”

Of course, to make use of fibres as engineering materials they must be held together by a matrix. The material is then a two-phase structure or composite with a combination of properties from both constituents. However, the aim is to provide the composite with the advantageous properties of the fibre. Matrix materials and composites are discussed later.
The first material to be used in fibre form was glass in the late 1930’s and glass continues to be the most widely used reinforcement for plastics today. Glass fibre has a high strength, ready availability, low density and low cost. The four most common glasses used for glass fibres are alkali glass (A-glass), electrical grade (E-glass), a modified E-glass that is chemically resistant (ECR-glass) and high strength glass (S-glass). S-glass has the highest tensile strength and modulus and highest temperature property retention. Glass may be formed into continuous or discontinuous fibres.

In the late 1950’s ceramic materials were produced in whisker form. These single crystal ceramics, virtually free from defect, exhibited exceptionally high strength and stiffness but unfortunately are very costly to produce. The ceramics used as fibres are compounds of the lighter elements in the periodic table including Al₂O₃, BeO, SiC, SiO₂ and B₄C. Such fibres have stiffness values of five times that of glass fibres, improved strengths, are lightweight and possess good refractory properties. However such whiskers are difficult to mount in a matrix in terms of getting specified alignments and constant number of fibres per unit volume. Some of these materials can also be made into continuous fibres. Continuous fibres can also be manufactured from synthetic organic materials and metals (metallic wires).

Carbon fibres are of most interest in this project. Carbon whiskers with very high strengths and tensile moduli may be produced but again these are difficult to mount in a composite. Continuous carbon fibres with strengths and moduli larger than any other materials can now be produced. Carbon fibres are low in cost to produce and have the advantages of the properties of carbon such as low density, chemical inertness and refractory properties of retaining strength up to 2000°C and above.

Table 2 [42-45] summarises the properties of a range of continuous fibres and table 3 [45] compares the properties of some short fibres and whiskers.
Table 2. Properties of Continuous Fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (HM), P100</td>
<td>2.15</td>
<td>2.24</td>
<td>724</td>
</tr>
<tr>
<td>Carbon (HT), T40</td>
<td>1.74</td>
<td>4.5</td>
<td>296</td>
</tr>
<tr>
<td>S-glass</td>
<td>2.5</td>
<td>4.6</td>
<td>84</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.63</td>
<td>3.5</td>
<td>73</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.44</td>
<td>2.8</td>
<td>133</td>
</tr>
<tr>
<td>SIC</td>
<td>3.0</td>
<td>3.9</td>
<td>400</td>
</tr>
<tr>
<td>Boron-Tungsten</td>
<td>2.6</td>
<td>5.5-7.0</td>
<td>400</td>
</tr>
<tr>
<td>Boron-Carbon</td>
<td>2.3</td>
<td>5.0</td>
<td>400</td>
</tr>
<tr>
<td>α-alumina</td>
<td>3.95</td>
<td>14-19</td>
<td>390</td>
</tr>
<tr>
<td>Metallic Wires</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.71</td>
<td>0.29</td>
<td>68.9</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1.85</td>
<td>1.1</td>
<td>310</td>
</tr>
<tr>
<td>Copper</td>
<td>8.9</td>
<td>0.413</td>
<td>124</td>
</tr>
<tr>
<td>Tungsten</td>
<td>19.3</td>
<td>2.89</td>
<td>345</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>7.9</td>
<td>2.39</td>
<td>200</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>10.2</td>
<td>2.2</td>
<td>331</td>
</tr>
</tbody>
</table>

Table 3. Properties of Continuous and Discontinuous Fibres

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina whiskers</td>
<td>4.0</td>
<td>10-20</td>
<td>700-1500</td>
</tr>
<tr>
<td>Alumina fibres</td>
<td>&lt;4.0</td>
<td>0.2-0.7</td>
<td>140-300</td>
</tr>
<tr>
<td>Boron whisker</td>
<td>2.3</td>
<td>2.75</td>
<td>400</td>
</tr>
<tr>
<td>Boron nitride fibre</td>
<td>1.8-2.0</td>
<td>0.3-1.4</td>
<td>28-80</td>
</tr>
<tr>
<td>Carbon whiskers</td>
<td>&gt;2.0</td>
<td>~20</td>
<td>~700</td>
</tr>
<tr>
<td>Carbon fibres</td>
<td>1.8-2.15</td>
<td>2.0-4.8</td>
<td>230-724</td>
</tr>
<tr>
<td>Silicon nitride whiskers</td>
<td>3.2</td>
<td>5-7</td>
<td>350-380</td>
</tr>
</tbody>
</table>

In each case the whiskers have a higher tensile strength and modulus because of their near perfect atomic arrangements and low surface imperfections.

Carbon fibres may be produced from three different precursors which are discussed in the following section. The microstructure of carbon fibres is then examined and the mechanical properties of carbon fibres are discussed in more detail. A brief outline of fracture mechanics applied to carbon fibres is given and finally types of carbon fibre cloth used in composites are described.
2.6.2 Carbon fibres produced from different precursor materials

Carbon fibres are produced from three types of precursor material: rayon, polyacrylonitrile and pitch. All three types are discussed here.

2.6.3 Rayon-based carbon fibres

In 1878 Thomas Edison transformed cellulose based materials, namely cotton and later bamboo strips, into carbon for use in incandescent electric lamps. However, when the lamp industry converted to using tungsten filaments, carbon fibre production ceased. The next interest in carbon fibres came in the late 1950's when the discovery that graphite whiskers, made using a D.C. arc between carbon electrodes in an inert atmosphere under 9MPa of pressure, had strengths of 20GPa and moduli of 1000 GPa. Subsequently the Union Carbide Company fabricated the first carbon fibres from rayon (cellulose) with strengths of up to 275 MPa and these were closely followed by fibres with strengths up to 700 MPa and moduli between 30-50GPa.

Nowadays rayon based carbon fibres only account for 1 wt % of all carbon fibre produced because they are not competitive in the market place for reasons that will later be revealed.

The main stages in production of carbon fibres from rayon are illustrated in figure 21 below.

Figure 21. Basic steps required to produce carbon fibres from rayon [1]
The cellulose fibres are initially produced by wet spinning. They are then oxidised at temperatures of around 500°C in an air or oxygen in nitrogen atmosphere. This oxidation step involves polymerisation and formation of cross links. It acts to convert the rayon into a form that will be stable at higher heat treatment temperatures which the next stage of processing requires. Before this first stage oxidation procedure the rayon may be subjected to a chemical treatment in aqueous ammonium chloride solution or dilute phosphoric acid in denatured ethanol. This chemical treatment reduces the time required for the low temperature step from several hours to around 5 minutes. Between 50 and 60% of the fibre mass is lost as decomposition products such as tars, H₂O, CO and CO₂ at this stage. Fibres produced from rayon have a characteristic crenulated surface like the original precursor.

The next stage of production is carbonisation in an inert atmosphere at around 1500°C. The carbon yield after this stage is 20-25% of the original polymer weight. At this stage the fibres are essentially isotropic and there is poor alignment of the graphene layers which results in poor mechanical properties. The final stage is graphitisation at 2500-3000°C which improves the orientation of graphene layers. Fibres may be stretched during the graphitising stage to further increase graphene orientation and thus strength and modulus but this is expensive. The tensile modulus of the graphitised fibre is directly related to the graphitisation temperature and the stretch ratio used.

The combination of poor mechanical properties, low carbon yield and expense of graphitisation are the reasons, alluded to above, why rayon based carbon fibres are not competitive in the market place. Typical properties of rayon-based fibres are shown in table 4 below.
Table 4. Typical properties of rayon based carbon fibres [1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Tensile strength</td>
<td>1.0 GPa</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>41.0 GPa</td>
</tr>
<tr>
<td>Elongation to break</td>
<td>2.5%</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>20 Ωm</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>1.6 g cm⁻³</td>
</tr>
<tr>
<td>Fibre diameter</td>
<td>8.5μm</td>
</tr>
<tr>
<td>Carbon assay</td>
<td>99%</td>
</tr>
</tbody>
</table>

2.6.4 PAN-based carbon fibres

In the mid 1960's it was discovered that polyacrylonitrile or PAN fibres could be made into carbon fibres with superior mechanical properties to those made from rayon by using an oxidation stage prior to carbonisation [46]. PAN based fibres now account for 90% by weight of all carbon fibres being produced.

The major steps in the production of PAN based fibres are shown in figure 22 below. This figure also includes the manufacture stages for pitch based carbon fibres, which are discussed in the next section, for comparison.
The fibres are first heated to 200-300°C in an oxygen containing atmosphere such as air, oxygen or ozone enriched air or sulphur dioxide or nitrogen dioxide to stabilise them ready for carbonisation. During this oxidative process the nitrile groups react to form a closed ring structure (this reaction is very exothermic and must be controlled by use of a temperature that does not allow catastrophic runaway of the exothermic reaction) and the oxygen aids cross linking of the chains. This process may be done in tension to maintain the orientation of the graphene layers.

Carbonisation, which takes about 1 hour, is carried out at 1000-1500°C and the fibres now undergo both chemical and physical transformations. Around 50% by weight of the fibre is lost as H₂O, NH₃, HCN, CO, CO₂, N₂ and possibly CH₄ and the fibres are bathed in their own decomposition products. Carbonisation is carried out in nitrogen or argon to dilute these waste gases before extraction and also to prevent oxidation. After carbonisation the fibre is about 45-50% carbon by weight.
Physically the fibre has been transformed from a low strength and modulus, high extensibility (strain to failure) fibre to a brittle, high strength and modulus, low extensibility fibre. The density of the fibres increases and the fibre diameter decreases.

The final stage is graphitisation which is not always used, depending on what type of fibre is required. This process is carried out in an inert atmosphere. There is little evolution of gas and the main changes are in the physical structure of the fibre. Microcrystallites grow in size and preferred orientation of the graphene planes is achieved. Tension may again be applied to further improve the crystallite alignment and hence the fibre modulus, as long as overstretching is avoided as this could break the fibre. Graphitisation only takes a few minutes.

PAN based carbon fibres vary in mechanical properties with respect to their heat treatment temperature (HTT) as illustrated in figure 23 below.

Figure 23. Strength and modulus of PAN based fibres for various heat treatment temperatures [1].
Three zones of HTT lead to three types of Pan based fibre:

(1) **Low modulus, LM, fibres (Type III)**

Zone 1, up to 1000°C, is the carbonisation region in which the fibres undergo their main thermo-chemical degradation losing up to 50% of their weight but no physical degradation occurs in this zone. There is a residual amount (4-8%) of nitrogen in the fibres. Fibres produced after carbonisation alone are low modulus fibres with moduli from 190-220 GPa. In this region strength increases proportionately with modulus.

(2) **Intermediate modulus, IM, fibres (High strength fibres) (Type II)**

Zone 2 is the region from 1000-1500°C. Very little chemical change occurs here except the expulsion of nitrogen. Physically, the crystallites grow and graphene layers begin to further align. The shallow curvature of the modulus curve shows that the contribution to degree of alignment is as much to do with the amount of alignment in the original fibre as from increased temperature. The average angle of alignment of graphene layers to the fibre axis is 30° at this stage, leading to intermediate modulus type fibres with moduli from 220-250 GPa. These fibres have the highest tensile strength and highest extensibility (1.2-1.8%) and are preferred in aircraft and car manufacture. The strength normally exceeds 1% of the modulus value (strain to failure value is 1.2% or greater). The strength in this region is thought to be controlled in terms of fracture mechanics by surface, and possibly internal, flaw mechanisms.

(3) **High modulus, HM, fibres (Type I)**

Zone 3 is the graphitisation region in which further improvements in orientation and hence modulus are achieved. Moduli between 360-400 GPa are reached in this zone. In this zone the strength actually begins to decrease as flaw mechanisms become obscure and the graphitic structure contributes significantly to strength (more perfection and more layer alignment leads to reduced strengths). Some workers have reported a steady increase in strength with HTT in this zone but the modulus always
increases proportionately faster such that the strain to failure value always decreases in this region.

As HTT is increased throughout all three zones the density of the fibres also increases. Typical properties of PAN-based fibres are shown in table 5.

Table 5. Properties of carbon fibres from PAN precursors.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Low Modulus (LM)</th>
<th>Intermediate modulus (IM)</th>
<th>High modulus (HM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength (GN m⁻²)</td>
<td>3.3</td>
<td>4.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Tensile modulus (GN m⁻²)</td>
<td>230</td>
<td>270</td>
<td>390</td>
</tr>
<tr>
<td>Elongation to break (%)</td>
<td>1.4</td>
<td>1.7-1.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>8.5</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Electrical resistivity (Ωm)</td>
<td>18</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>CTE at 21°C (10⁻⁶ K⁻¹)</td>
<td>-0.7</td>
<td>-</td>
<td>-0.5</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus (GN m⁻²)</td>
<td>40</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>CTE at 50°C (10⁻⁶ K⁻¹)</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.76</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Fibre diameter (μm)</td>
<td>7-8</td>
<td>6-7</td>
<td>4-6</td>
</tr>
<tr>
<td>Carbon assay (%)</td>
<td>92</td>
<td>96</td>
<td>100</td>
</tr>
</tbody>
</table>

2.6.5 Pitch-based carbon fibres.

The first pitch based carbon fibres were developed in the early 1960's by Otani and co-workers [47]. They were developed using isotropic pitch using a method similar to that used for PAN fibres, also show in figure 22. The isotropic pitch is first pyrolysed between 300-500°C and then melt spun into fibres. The pitch fibres are then oxidised to cross link and stabilise them before carbonisation and graphitisation stages. The
oxidation is, as for PAN fibres, highly exothermic and the rate limiting step. Fibres made from the isotropic pitch exhibit only modest mechanical properties with a Young’s modulus of around 40 GPa and strength of 0.8 GPa as a direct result of their isotropic nature. Stretching the fibres at graphitisation temperatures of 2200-2900°C, as done by Hawthorne [48], improved graphene layer alignment and strengths up to 2.6 GPa and moduli up to 620 GPa were achieved. However this hot stretching is a very difficult and expensive process and was not taken up commercially because the cost advantage of using inexpensive pitch as the fibre precursor is outweighed by the processing costs. However pitch based fibres are in production for use in low modulus applications such as in plastic fillers in thermal insulation, heating elements, pump packings and as cement reinforcement due to their resistance to alkali attack. Typical properties of isotropic pitch-based fibres are shown in table 6.

Table 6. Properties of carbon fibres from pitch precursors [1].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength (GN m⁻²)</td>
<td>1.0</td>
</tr>
<tr>
<td>Tensile modulus (GN m⁻²)</td>
<td>41</td>
</tr>
<tr>
<td>Elongation to break (%)</td>
<td>2.5</td>
</tr>
<tr>
<td>Electrical resistivity (Ωm)</td>
<td>20</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.6</td>
</tr>
<tr>
<td>Fibre diameter (μm)</td>
<td>8.5</td>
</tr>
<tr>
<td>Carbon assay (%)</td>
<td>99</td>
</tr>
</tbody>
</table>
In 1971 Otani developed the first carbon fibres from mesophase pitch. Mesophase is anisotropic in nature compared to the isotropic pitch and so it was predicted that a high performance fibre could be achieved. The same method as for the isotopic pitch was used, starting with melt spinning. There are several reasons why mesophase pitch had the potential to yield a high performance fibre at a lower cost than PAN fibres. Firstly, the isotropic pitch precursor is about 1/5 the price of PAN. Secondly tension is not required at the oxidation stage as the melt spinning process imparts a high degree of molecular orientation to the fibre. Thirdly, the mesophase pitch fibre begins with a structure closer to graphite than PAN so it requires less energy to convert to an axially aligned, high modulus fibre and hence lower temperatures and residence times are required for carbonisation. Finally mesophase pitch has fewer heteroatoms than PAN and so the carbon yield is higher (75-95% compared to 45-50% for PAN fibres and 20-25% for rayon fibres) and the process more efficient.

Unfortunately the cost of producing fibres from mesophase is enhanced by the extensive purification of the precursor to remove flaw inducing particles and also by the melt spinning process that is far from conventional for pitch mesophase. Thus mesophase pitch fibres are only able to compete with PAN fibres at the high modulus (>400 GPa) end of the market. Typical properties of mesophase pitch-based fibres are shown in table 7.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Low Modulus (LM)</th>
<th>Intermediate modulus (IM)</th>
<th>High modulus (HM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Axial</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength (GN m(^{-2}))</td>
<td>1.4</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Tensile modulus (GN m(^{-2}))</td>
<td>160</td>
<td>380</td>
<td>725</td>
</tr>
<tr>
<td>Elongation to break (%)</td>
<td>0.9</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal conductivity (W m(^{-1}) K(^{-1}))</td>
<td>-</td>
<td>100</td>
<td>520</td>
</tr>
<tr>
<td>Electrical resistivity (Ωm)</td>
<td>13</td>
<td>7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>CTE at 21°C (10(^{-6}) K(^{-1}))</td>
<td>-</td>
<td>-0.9</td>
<td>-1.6</td>
</tr>
<tr>
<td><strong>Transverse</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus (GN m(^{-2}))</td>
<td>-</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>CTE at 50°C (10(^{-6}) K(^{-1}))</td>
<td>-</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td><strong>Bulk</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>1.9</td>
<td>2.0</td>
<td>2.15</td>
</tr>
<tr>
<td>Fibre diameter (μm)</td>
<td>11</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Carbon assay (%)</td>
<td>&gt;97</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>
2.7 Methods Used to Determine the Microstructure of Carbon Fibres

There are several review articles [49-52] on the microstructure of carbon fibres. In this section, the techniques that are used to elucidate the microstructure of carbon fibres are described. The section then reviews many of the models used to describe the microstructure of carbon fibres.

2.7.1 X-ray and electron diffraction

These methods are used to determine a number of structural properties of carbon fibres including the type of crystal planes present, interlayer spacing, crystallite size and preferred orientation of crystallites. Diffraction from regular atomic planes in a crystalline solid occurs at diffraction angle \( \theta \) when the Bragg condition (equation 1 below) is satisfied:

\[
2d \sin \theta = m\lambda \quad (1)
\]

where \( d \) is the inter-layer spacing and \( \lambda \) is the wave length of the incident beam.

X-rays have greater penetrating power than electrons and are used to obtain a diffraction pattern from a bundle of fibres or a single fibre.

A transmission electron diffraction pattern can only be obtained from a thin section of 30-60 nm.

Diffraction from a single crystal produces a diffraction pattern of spots. If many crystals are present there is a range of orientations of each type of crystal plane relative to the incident beam and a number of spots are produced per crystal plane type which merge to form arcs or continuous circles.

2.7.2 Determination of the planes that are present in the carbon fibre and the interlayer spacing.

An X-ray or electron beam perpendicular to the fibre axis will produce reflections from the layer planes aligned parallel to the fibre axis. Figure 24 shows a diffraction pattern from a thin flake of carbon fibre and the set of crystallographic planes from which the reflections arise.
Figure 24. Electron diffraction pattern from a thin flake of a high modulus carbon fibre. Four of the crystallographic planes are illustrated [46].

Reflections from (002) planes are the most intense showing that there are more of these planes present than any other. Reflections such as (112) from three-dimensional graphite are rarely found in carbon fibres due to the lack of three-dimensional order in them. The layer spacing, d, can be obtained from the diffraction angles, θ, substituted into the Bragg equation.
2.7.3 Determination of crystallite size

Reflections from large crystallites are sharp but broaden when crystallite size is reduced or there are changes in the spacings between diffracting planes (e.g. from microstrain or dislocations). The crystallite size can thus be calculated from the width of the reflection using the Scherrer equation (equation 2):

$$L = \frac{K\lambda}{b \cos \theta}$$  (2)

where

- $K$ is a constant ($\approx 1$)
- $\lambda$ is the wave length of the incident beam
- $b$ is the half width of the broadened reflection
- $\theta$ is the diffraction angle
- $L$ is the linear dimension of crystallite at angle $\theta$ to the incident beam

2.7.4 Determination of the preferred crystallite orientation

The angle of spread of the (002) reflection (i.e. the range of angles of the (002) diffraction arc) allows the preferred orientation to be measured. To do this the intensity, $I(\theta)$, at different angles, $\theta$, on the diffraction arc, is measured. It has been shown that $\phi$, the angle of the crystallite c-axis (axis perpendicular to the layer planes) relative to the fibre axis (figure 25) is related to the diffraction angle, $\theta$, via equation (3).

$$\cos \phi = \cos 13^\circ \cos \theta$$  (3)
Figure 25. Schematic diagram of a carbon fibre to show the c-axis and $\phi$ direction.

The intensity due to each orientation of layer planes, $\phi$, is a function of the number of layer planes at $\phi$ causing the reflection.

A plot of $I(\phi)$ versus $\phi$ shown in figure 26 is bell shaped with a narrow distribution centred on the fibre axis. This indicates the high degree of orientation of (002) planes along the fibre axis.

Figure 26. A plot of $I(\phi)$ versus $\phi$ [53].
It can be shown that:

\[ I(\vartheta) \approx \sin^m \phi \quad (4) \]

where \( m \) is an anisotropy factor (\( m = \text{ratio of properties parallel to properties perpendicular to the fibre axis} \)). The higher the value of \( m \), the higher the degree of layer plane orientation along the fibre axis.

For soot \( m=1 \) and for extruded Ceylon \( m=5 \) and for carbon fibres \( m \) can have values of up to 100 which illustrates a high degree of layer plane orientation along the fibre axis.

Other orientation factors have been described but the half width at half maximum of the intensity plot of the \( (002) \) diffraction beam is a good measure of preferred orientation.

2.7.5 Optical microscopy

Cross sections and longitudinal sections of polished carbon fibres can be examined under the light microscope. Cross sections show fibre shape and longitudinal sections show feature such as holes. However, the magnification is limited to \( \times1500 \) and depth of focus is small. Polarised light and a full wavelength retarder plate at 45° between the polariser and analyser produce interference colours due to anisotropy and hence show orientation of surface crystallites.

2.7.6 Scanning electron microscopy (SEM)

This method is used for fractography i.e. for examining fracture surfaces of carbon fibres. It has a greater magnification and depth of field than optical microscopy with magnifications up to \( \times5000 \) and \( \times10000 \). Such magnifications can show the initiation point of fracture and some structural details. It has been shown, for example, that HM fibres have more fibrous fracture surfaces than LM fibres. Polished sections show no structural features but chemical etching produces patterns from which the structure may be deduced.
2.7.7 Transmission electron microscopy (TEM)

The resolving power of a lens is related to the lens aperture size and wavelength of illumination. TEM allows magnifications of up to $1 \times 10^5 - 2 \times 10^5$ when the wavelength of electron beams is 0.004 nm at 100 kV. This magnification allows good imaging of carbon fibres. A diffraction pattern on the other side of the specimen from the incident beam, is formed.

Fibre specimens must be less than 100 nm thick so fibres that are about 8 μm diameter cannot be examined directly. The edge structure of such fibres can be imaged and fibre fragments obtained by grinding have been used. However the position of ground fragments is not known and the best specimens to use are thin sections cut on an ultramicrotome with a diamond knife. Longitudinal sections of 30-60 nm thick can be cut but transverse sections are more difficult to prepare.

2.7.8 Bright field imaging

A TEM bright field image of a carbon fibre is shown in figure 27. This image is produced from all the reflections when the objective lens aperture is positioned centrally and selects the direct beam.
Figure 27. Bright field image of a thin section of carbon fibre and its diffraction pattern [49].

Many crystallites are present so contrast in the image is caused by diffracted beams being stopped by the lens aperture. Contrast is also induced by beam attenuation due to variation in section thickness. These micrographs thus require very careful interpretation.

2.7.9 Dark field imaging

A TEM dark field image of a carbon fibre is shown in figure 28. In this method the electron beam or the specimen is tilted so only a selected diffraction angle beam is brought into the centre position, usually occupied by the direct beam.
Figure 28. (002) dark field electron micrograph of a thin section of carbon fibre [49].

For example, if the (002) diffraction angle is selected, only crystallites orientated with the (002) plane at this angle to the incident beam will diffract electrons down the axis of the microscope and appear as bright areas on the image. From this, the orientation of the crystallites can be deduced.

2.7.10 High resolution electron microscopy

In optical microscopy, phase contrast is produced by retarding the unscattered direct beam by $\pi/2$ and then making it interfere with the unretarded scattered beam so that contrast produced in the image corresponds to the phase differences in the object. In the electron microscope, the same principle may be used to produce high resolution images of structure.

The degree of defocus of the objective lens, a phase shift is obtained between the scattered (diffracted) waves, which take a longer path through the lens and the unscattered waves. Spherical aberration of the lens reduces the phase shift. The total path length difference and hence the phase shift between the waves depends on the scattering angle, the spherical aberration coefficient of the objective lens and the degree of defocus used to produce the image.
2.8 Microstructure of Carbon Fibres

Early work on the structure of carbon fibres showed that the basic structural units of carbon fibres are the hexagonal graphite-like basal planes [46]. The Young's modulus of the fibre is a function of the proportion of graphene layers ordered parallel to the fibre axis. Also the lack of hkl diffraction spots indicated a lack of three dimensional order in the graphene planes. The layers are parallel to each other but are not ordered with respect to each other. Materials that consist of extended graphene layers but do not possess the complete three dimensional graphitic structure, including carbon fibres, are defined as having "turbostratic" structures. Some regions of three dimensional graphite were also seen in the carbon fibres. These facts were established but the micromorphology in terms of the arrangement and interconnection of the layers in the transverse direction that was uncertain.

In 1969 Johnson and Tyson [54] proposed a model, shown in figure 29, for the structure of PAN-based carbon fibres from their studies on high and low angle X-ray diffraction.

![Figure 29. Carbon fibre structure with columnar arrangement of misoriented turbostratic crystallites forming tilt and twist boundaries. (S₁ = void, S₂ = sub-grain, S₃ = inter-crystalline boundary) [54].](image)
This structure consists of misorientated turbostratic graphitic crystallites with crystallite dimensions $L_a$ and $L_e$ of about 6.5nm stacked end to end in columns. There are sharp tilt and twist boundaries between them leading to sharp-edged voids between them. The mean width of voids is less than 1 nm. This model was simple and fitted the diffraction data but it required modifications. Firstly, to account for the high strength of the fibres perpendicular to the fibre axis, there needed to be some form of linking between the crystallite strings. Secondly, dark field electron micrographs such as the one in figure 30 had shown units which were longer than the $L_a$ measured by diffraction. When a thin section was tilted in the microscope, the units were seen to twist along the length of the fibre suggesting that the structure was not a series of unconnected cells.

Figure 30. Electron micrograph of a thin section of a carbon fibre cut across the fibre axis. Fibre carbonised to 1000°C only [55].
Later, in 1971, Johnson et. Al. [56] did some work on high modulus PAN fibres and developed the block model into the more complex model shown in figure 31.

![Figure 31. More complex model for carbon fibres developed from the block model.](image)

This model incorporates vertical arrangements of subgrains in agreement with the model by Johnson and Tyson. It consists of interlinked crystallites, sharp edged voids and imperfect stacking with twist boundaries. The interlinking accounted for Moiré patterns seen in bright and dark field images (figure 32) which are caused by overlap of layers.
Figure 32. (002) dark field micrograph of a thin section of a carbon fibre made from PAN. The skin, 100 nm thick, is shown. Moiré Patterns are clear [57].

Studies by Ruland and co-workers on X-ray diffraction and electron microscopy of carbon fibres lead to their proposal of a microfibrillar structure (figure 33).

Figure 33. Microfibrillar structure of carbon fibres [58].
Ruland [58] and Fourdeaux [59] found no evidence for the existence of sharp grain boundaries transverse to the ribbon direction. A number of other studies also excluded the possibility of such boundaries and supported the microfibrillar structure. In their proposed structure a number of ribbons of carbon fibres group together to form a wrinkled microfibril with a high degree of preferred orientation parallel to the fibre axis with a spread of ±10°. This model still fits in with the structure seen in dark field electron micrographs consisting of smoothly curved microfibrils (figure 32) and Moiré patterns caused by superposition of two layers. The fibrils have a width of about 10 nm and length of several hundreds of nm. The values of crystal dimensions Lc and Lw had already been measured by X-ray diffraction to be between 6-12nm. The value Lc was now shown to consist of 12 layer planes. The small value for Lw was the result of the X-ray method which only measures the straight portion of the long fibrils. The interlayer spacing was found to be 0.339 nm compared with 0.335 nm, the value for natural graphite. Irregular contours of the ribbons lead to voids between the ribbons that are 20-30nm long and 1-2 nm across. These voids follow the orientation of the ribbons and the sharpness of density transition between the pore and carbon material suggests that the pore walls are carbon layer planes.

Earlier Herinckx et. Al. [60] reported that carbon fibres could form intercalation compounds with potassium without damage to the micromorphology so suggesting that there are no diamond like carbon bonds acting as cross links between the layer planes. This lead to the suggestion that the strength of the fibres was due to branching and interweaving of the ribbons, not cross linking.

Diefendorf and Torkarsky [61] proposed the basket weave ribbon structure in figure 34.
Figure 34. Basket weave ribbon structure model for carbon fibres [61].

In this model the curvature of the ribbons have near-zero amplitude and the ribbons are essentially parallel to the fibre axis. The overall structure is thus sheet like, as has been seen in a number of TEM pictures.

Bennett and Johnson [62,63] put forward the two dimensional model of the three dimensional crystallite in figure 35. This includes some crystallite interlinking that explains the torsional rigidity that would be lacking if the fibres contained fibrils, in a rope like structure.

Figure 35. Two dimensional representation of crystallite interlinking in a carbon fibre [62,63]
Oberlin [64] has recently proposed a model for the high strength and high modulus PAN based carbon fibres. The only difference in the two types of fibre is the transverse radius of curvature of layers which is larger for high modulus fibres.

2.8.1 Lamellar model

There have been several studies that suggest that carbon fibres have a lamellar structure as well as or instead of the fibrillar structure. The first detection of a lamellar structure was by Shindo [65] as a result of electron diffraction studies. Johnson and co-workers [66] first observed a lamellar structure on examination of the fracture surfaces using SEM. PAN-based carbon fibres that were partially oxidised, then carbonised and graphitised at 2000°C showed a lamellar structure within the fibre which developed at higher graphitising temperatures and it was found that the lamellar structure was a function of the graphitisation temperature. The lamellar structure developed throughout the fibre at a temperature of 2560°C, converting some fibrillar structure into lamellar structure. It was found that the development was due to the partial stabilisation of the fibre since fibres that had been fully stabilised showed no lamellar structure. The lamellar structure has an $L_e$ value of 230 nm compared to the 10 nm of the fibrillar structure.

In another study by Johnson [67] a lamellar form was observed in stress-graphitised carbon fibres. The method of development of the lamellar structure in this case is obviously different to that in the partially stabilised fibres but the final structure was the same indicating that the lamellar structure is the final stable form of carbon fibres.

Other studies have observed lamellar structures including [68] and [69]. The second of these studies found a lamellar structure in fibres that had already been shown to possess a fibrillar structure. Probably, the fibrillar structure gradually changes into a lamellar one as the preferred orientation increases. So a carbon fibre can simultaneously possess a fibrillar and lamellar structure and the fibrillar structure may, under certain conditions, convert into a lamellar form which is believed to be the most stable structure. Fibrillar and lamellar structures are similar in that if a
lamella is small enough, it looks like a fibril and if a fibril is large enough it looks like a lamella.

2.8.2 Cross sectional structures

Cross sectional structures are important in determining the three dimensional structures of carbon fibres. Knibbs [70] identified three types of cross sectional structures (figure 36) which differ in orientation of the graphitic crystallites in the transverse plane. Structures (a) and (b) have two zones. Structure (a) has an outer zone with circumferential orientated crystallites and an inner zone which is almost completely isotropic.

![Figure 36. Schematic representations of transverse cross section of carbon fibres. (a) Isotropic centre and oriented skin. (b) Different orientations in the centre and outer layers. (c) One type of preferred orientation [70].](image)

Structure (b) has an outer layer of orientated crystallites and an inner zone with radially preferred orientation. Structure (c) has circumferentially oriented crystallites throughout. The type of structure depends on processing conditions but is independent of heat treatment temperature which just serves to increase the longitudinal alignment, whichever the transverse orientation.

Diefendorf and Le Maistre [71] described an onion-skin structure with a circumferential outer zone which graduates into a gradually more misaligned
structure further towards the core of the fibre. Barnet and Norr [72] proposed the “Circumferential-Radial” Model shown in figure 37.

![Diagram of the Circumferential-Radial model](image)

Figure 37. Circumferential-radial model [72].

This model consists of a sheath with circumferential orientation of crystallites which moves into a radial continuum towards the core and includes holes and cracks. These workers proposed that the precursor type was important in the transverse section of the carbon fibre. This structure is thought to be a complete model of all possible features of a carbon fibre but is in fact an extreme structure. Not all carbon fibres will possess all the features of this model.

Diefendorf and Torkarsky [61] also observed the radially preferred orientation in carbon fibres. They propose that the texture in the core of the fibre does depend on
the processing conditions but the surface always has an onion-skin structure. Where there is a change from one ordered structure to another from skin to core then this structure is dependent on processing conditions, for example, spinning conditions where differential shear rates across the fibre diameter account for the different structures.

Wicks and Coyle [73] agree that the skin always has a circumferential preferred orientation. They found that the inner region structure is dependent on diameter of fibre. The thinner fibres had more circumferential orientation whereas thicker fibres had more isotropic, randomly aligned material. Where the inner core of the fibre consists of randomly structured material it is probably due to the extent of stabilisation of the material in the fibres. The thicker fibres are more likely only to have been partially stabilised and so are less well ordered.
2.8.3 Three-dimensional models

Diefendorf and Torkarsky [61] have constructed three dimensional models for a rayon and two PAN-based carbon fibres as in figure 38.

Figure 38. Three dimensional models for three types of carbon fibre: (a) Rayon-based Wyb; (b) PAN-based Fortrail 4y; (c) PAN-based CS-1. [61]
The rayon based fibre in figure 38(a) has an axial structure of small microfibrils orientated at all angles to the fibre axis. The PAN fibres in figures 38(b) and 38(c) have complex internal radial structures with skins that have axially or circumferentially orientated crystallites, respectively.

Johnson's recent model (figure 39) [74] shows a gradual change from aligned crystallites at the surface to randomly aligned ones towards the middle. This model is consistent with a skin and core model as described before.

Figure 39. Carbon fibre three dimensional model showing change from aligned crystallites at the surface to randomly aligned ones towards the middle [74].

Oberlin has concluded that high tensile strength PAN fibres consist of structural unit less than 0.1 nm in size that are edge to edge forming large, wrinkled layers. The sheets are crumpled parallel to the fibre axis and the folds are entangled resulting in pores that elongate parallel to the fibre axis. High modulus carbon fibres are also described by the same model.
2.9 Mechanical Properties of Carbon Fibres

Carbon fibres were first developed for their low density and high stiffness (high Young’s Modulus). They have relatively low tensile strengths compared with other fibres and relatively low strain to failure. Their compressive strength is variable according to type of precursor and processing conditions, but is generally poor.

2.9.1 Tensile modulus

The theoretical value for the Young’s modulus of graphite is 1000 GPa compared to 300 MPa for organic polymers. The Young’s modulus of a carbon fibre is an intrinsic property of the fibre and it has been found by Fourdeaux et al [75] that there exists a correlation between the preferred orientation of graphitic layers and the Young’s modulus. This correlation is simply that the more highly orientated the layer planes, the higher the Young’s modulus. Figure 40 is a graph of the variation of tensile modulus with preferred orientation for a pitch based carbon fibre. For basal planes lying within ± 35° to the fibre axis, the Young’s modulus is 103 GPa and within ± 10° the modulus is 410 GPa.

![Graph of the variation of tensile modulus with preferred orientation](image)

Figure 40. The relationship between tensile modulus and preferred orientation for a pitch-based carbon fibre.
To align fibres parallel to the fibre axis requires a considerable input of energy. PAN fibres require more energy than pitch fibres since pitch is graphitising and PAN is non-graphitising. Thus the highest reported modulus of pitch based fibres is around 800 GPa [76] which corresponds to a preferred orientation of 5° whereas for PAN fibres it is difficult to achieve preferred orientation below 10° and modulus greater than 400 GPa [1].

Fourdeaux et. Al. explained this relationship in terms of the “wrinkled ribbon theory” of carbon fibres. Torkarsky and Diefendorf [77] observed significant deviations from the Fourdeaux plots which they explained by the existence of a gradient in preferred orientation through the cross section of the fibre. They propose the dog bone cross section which consists of a surface with near-perfectly axially aligned layers with poorly orientated material in the lobes and core of the dog bone. Stevens and co-workers [78] have observed a modulus gradient within the fibre with surface layers having higher moduli than core material. Dependence of fibre modulus on diameter has been observed by Jones and Duncan [79] and Perry et. Al. [80]. This is explained by the above suggestion of a dual structure. A larger proportion of thin fibre will be composed of sheath consisting of aligned material than thick fibres thus the thin fibre will have a higher modulus.

It has been found that stretching fibres, heat treatment temperature and boron doping and neutron irradiation all affect the degree of orientation and modulus.

2.9.2 Influence of stretch on tensile modulus

Stretching the fibre at some stage of its processing enhances fibre orientation and thus young’s modulus. It has been shown [81,82] that the modulus of the fibre can be controlled by the amount of stretch. PAN fibre stretching is carried out at the low temperature oxidation stage as has been investigated by a number of workers [82-86]. Elongated fibres have been shown to have higher moduli due to the parallel alignment of molecular chains during cross linked reactions. Pitch fibres are oriented during the spinning process but have also been shown to have increased modulus by hot stretching during graphitisation, [87,88], although high modulus pitch fibres can be produced up to 700 GPa without stretching. This is due to the high graphitisability of pitch compared to PAN or rayon. The degree of alignment that can be reached in pitch fibres are so high that the modulus of such carbon fibres begins to depend on structural defects rather than degree of alignment.
2.9.3 Influence of heat treatment temperature on tensile modulus

Increasing the heat treatment temperature increases the preferred orientation and thus the modulus, as has been investigated by a number of workers [89-92]. Figure 41 [1] shows the variation of preferred orientation with heat treatment temperature for pitch and PAN based fibres.

![Graph showing preferred orientation change with heat treatment temperature](image)

Figure 41. The preferred orientation of the graphene planes as a function of HTT and precursor type [1].

Both curves show a similar trend but the PAN fibre is 400°C higher indicating the higher input of energy required to achieve the same degree of orientation in PAN fibres as in pitch fibres.
2.9.4 Tensile strength of carbon fibres

Carbon fibres are a brittle material and their tensile strength, unlike their tensile modulus, is not an intrinsic property but is dominated by the presence of flaws and defects according to the Griffith theory as has been discussed in section 2.5.4. There have been many measurements of the strength of carbon fibres, usually using single filaments. Measured strengths show a scatter of around 25% [93]. This scatter results from the problems of measurement techniques but also because of the existence of different types and amounts of flaws in the carbon fibre.

Graphite whiskers are carbon fibres that are almost free of defects and thus have strengths of up to 21 GPa, but carbon fibres exhibit many types of flaws including dislocations, stacking flaws, metal particle inclusions and gross discontinuities which all lead to decreased strengths. The flaws in carbon fibres are randomly distributed as has been shown by the fact that increasing the gauge length of carbon fibres decreases the strength, simply due to the fact that the longer length will contain more flaws. Moreton [94] found that the average strength of a fibre actually decrease exponentially with gauge length.

Flaws can be divided into two types: surface flaws and internal flaws. Surface flaws have lower strength distributions than internal flaws and thus carbon fibres tend to fail by surface flaws. In fact, surface flaws determine the strength of carbon fibres that have been heat treated up to about 1000-1200°C. If surface flaws are removed by etching the strength of the fibre increases and it fails by internal flaws. Surface flaws include surface imperfections, fibril boundaries, bends and kinks in microfibrils and surface pits.

Internal flaws become important in fibres heat treated above 1200°C when the severity of most of the surface flaws have been moderated. Internal flaws are usually present as voids or inclusions in the precursor material and retain their geometry during processing. Types of internal flaws include central cavities, diconical voids, inclusions and needle shaped cavities.

The amount and type of fractures and thus strength of carbon fibre depends on type of precursor, processing conditions, heat treatment temperature and pre-oxidation conditions.

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2.9.5 Effect of heat treatment temperature on tensile strength

It has been observed [96-98] that strength of carbon fibres increases up to 1500°C and decreases at temperature higher than this as shown in figure 32. It is thought that the increase in strength up to 1500°C is due to the decrease in the amount of flaws. The decrease in strength after 1500°C has been attributed to contamination of the carbon fibre with silicon or other impurities into the fibre from the furnace at these high temperatures.

Johnson [99] attributes the decrease in strength above 1700°C to the elimination, at higher temperatures, of amorphous carbon which is responsible for cross linking. He believes that strength is a function of the cross linking and as cross linking decreases so strength decreases (and modulus increases). As amorphous carbon is eliminated cross linking decreases thus layer planes are more mobile and a more perfect structure results. Above 1900°C there is almost no cross linking and thus strength remains virtually constant.

Jones and Duncan [100] believe that the high heat treatment temperatures cause a specific type of flaw which causes the decrease in strength while Sharp and Burnay [102] concluded the decrease in strength beyond 1500°C is due to the presence of inclusions that, at these high temperatures, volatilise to form voids at which misoriented three dimensional graphite forms.

2.9.6 Effect of pre-oxidation and pre-oxidation conditions on tensile strength

Pre-oxidation increases strength of carbon fibres as it stabilises molecular chains and prevents them from cleavage. However if the pre-oxidation stage is too long then the strength begins to decrease [102]. Watt and Johnson [95] observed that shrinkage during pre-oxidation of fibres at 220°C leads to fibres with lower strengths than those that had been stretched. Since strength depends on the amount of flaws, shrinking must introduce flaws into the fibres and stretching must reduce the amount of flaws.
However, stretching the fibre with tensile loads beyond an optimum value causes the strength to decrease [103]. This is thought to be due to sudden elongation and bond rupture.

Stretching during other stages of processing also increases the carbon fibre strength. For example stretching during wet (steam) spinning [104] and stretching of the textile precursor both increase the strength of fibre.

2.9.7 Effect of fibre diameter on tensile strength

Many articles [12,100,105,106] have found that as diameter increases the tensile strength of the fibre decreases. Since tensile strength is influenced by the presence of flaws it could be inferred that as diameter increases so fibre volume increases and so number of flaws increases explaining the decrease in strength. However, Jones and Duncan [100] found no such relationship between diameter and strength below 1200°C but did observe the relationship above 1200°C. It is known that these higher temperatures introduce Mrozowski cracks and consequently decrease in strength is likely to be due to these cracks. More of these cracks will occur in the randomly oriented material and since larger diameter fibres contain a higher percentage of randomly orientated material in their cores than thinner fibres, so they will form more Mrozowski cracks and thus have lower strengths. Also in the randomly oriented material there will be more cracks perpendicular to the fibre axis. These cracks are more effective than ones aligned parallel to the fibre axis. These cracks are more effective than ones aligned parallel to the fibre axis. Again fibres with a larger diameter and larger percentage of random core material will have lower tensile strengths.

Hsing and Rowe [107] found no dependence of strength on fibre diameter but found that fibres with more uniform diameters had higher strengths, probably due to the more even distribution of stresses in the more uniform samples.
2.10 Fracture mechanics in carbon fibres: Tensile failure

In 1973 Reynolds [108] reviewed fracture mechanics in carbon fibres. He included discussion on a number of possible contributing factors to fracture mechanisms in carbon fibres. However he could not find a simple relationship between flaw diameter, fibre strength and surface free energy. This led to the proposal by Reynolds and Sharp [108] which has been reviewed by Johnson [109] that there is a shear limit within a crystallite in a carbon fibre after which fibre fracture will occur.

The basis of this theory is the idea that crystallites are weakest in shear stress on the basal planes. When shear stress is applied to planes oriented along the fibre axis, the stress can be relieved by cracking or yielding between basal planes but if there is a misoriented crystallite in the fibre structure the shear strain energy may be large enough to rupture the basal plane of the misoriented crystallite. Figure 42(a) [110] shows a misoriented crystallite locked into the fibre structure. Figure 42(b) shows the basal plane rupture along $L_{a\perp}$ and a crack forming along $L_{\perp}$ when tensile stress is applied.

Figure 42. Reynolds-Sharp mechanism of tensile failure. (a) misoriented layers linking two crystallites parallel to the fibre axis. (b) Tensile stress applied parallel to the fibre axis causes layer-plane rupture in direction $L_{a\perp}$, crack develops along $L_{a\perp}$ and $L_{\perp}$. (c) Further application of stress causes complete failure of misoriented crystallite. Catastrophic failure occurs if the crack size is greater than the critical size in either $L_{\perp}$ or $L_{a\perp}$ direction.
For the crack to propagate one of two conditions must be fulfilled:

1. The crystallite size in one of the directions of propagation of the crack \((L_c \text{ or } L_{a\perp})\) must be greater than the critical flaw size, \(a_{\text{critical}}\), defined in the Griffith theory of brittle fracture (section 2.5.4).

2. The crystallite in which failure initiates must be sufficiently continuous with neighbouring crystallites for the crack to grow to its critical size within these neighbouring crystallites and thus to propagate.

The first condition is not usually fulfilled because both \(L_c\) and \(L_{a\perp}\) are much smaller than \(a_{\text{critical}}\). The second condition is most likely to be satisfied in regions of enhanced crystallisation and misorientation around the original rupture.

Evidence for this theory was provided in a recent study by Bennett et al. [111] who studied the tensile failure of some old type I PAN-based carbon fibres containing many flaws. The fibres were stressed to failure in glycerol and the fracture ends were viewed using SEM and TEM. Internal flaws that were found not to initiate failure had walls of crystallites oriented mainly parallel to the fibre axis. Internal and surface flaws that did initiate failure often had large misoriented crystallites in the flaw wall. The continuity around these flaws gave rise to values of \(L_{a\perp}\) which exceeded the critical flaw size and resulted in failure.

Further proof of the theory comes from an earlier study of lignin-based carbon fibres [112]. These fibres had very poor tensile strengths. They were found to have flaws in the form of catalytically graphitised regions around impurity particles in the precursor as shown in the TEM of figure 43(a) and the schematic drawing of this TEM in figure 43(b).
Figure 43. (a) TEM image of longitudinal section of lignin-based carbon fibre showing graphitic inclusion (b) Schematic representation of graphitic inclusion of (a). Arrow represents propagation of crack.

These regions were continuous with the rest of the fibre structure. Under stress misoriented crystallites in the inclusion failed and the crack propagates into the wall around the inclusion leading to total failure.

This theory explains why HM PAN fibres that have been treated to the highest heat treatment temperatures of 1990 -3000°C (zone 3 in figure 32) and HM pitch fibres have reduced strengths. The high heat treatment temperature has caused a high degree of alignment in such fibres which accounts for their high moduli. This high degree of orientation leads to fewer misoriented crystallites that can possibly initiate failure but increases the average size of crystallites such that it is more likely that the crystallite size exceeds $a_{\text{critical}}$ and any flaw within such a large crystallite will lead to catastrophic failure.
2.11 Carbon Fibre Cloth

Carbon fibre cloth can be made from continuous fibres into woven fabrics or from discontinuous fibres into felts or mats.

Short chopped fibres can be made into fibrous webs or felts. These felts are densified into composites by CVD or liquid impregnation followed by pyrolysis. Such composites are used in car brake manufacture. An alternative method of making cloth from discontinuous fibres is to initially impregnate continuous fibre tows which are then chopped and compression moulded into the required shape.

Continuous fibres may be made into unidirectional tape of 50-1000mm width or alternatively woven into cloth that is usually produced between 1 and 3 m in width. Unidirectional tape has negligible strength in the direction normal to the fibres and cannot be stretched over 2-dimensional structures. Woven fabric can be draped over 2-dimensional structures and their properties can be varied by selection of yarn and weave-types.

The long axis of carbon fibre cloth is defined as the y-axis and is known as the ‘warp’ direction. The warp direction is usually 30-150m long. The warp yarns are known as ‘ends’. The width of the cloth is the x-axis or ‘fill’ direction which is 0.9-3m wide. Fill yarns are called ‘picks’. A fabric is defined by the number of ends and picks per unit length and a weave is said to be balanced if these are equal. If these numbers are different then the weave is unbalanced and the extreme case of an unbalanced weave is a unidirectional tape with very little fill yarn to keep the warp yarns together.

There are three types of weave and the first, is the plain weave illustrated in figure 44. A plain weave consists of picks and ends going over and under each other such that there are equal amounts of warp and fill yarn on each side of the fabric. In this plain weave the yarns are interlaced at 90° to each other. Fabrics that are not woven at 0/90° to each other are called angle ply fabrics.
Figure 44. Illustration of a plain weave to show the warp and fill directions.

The fibres are clearly curved and deformed due to the weave. This deformation is called crimp. A tensile load would tend to straighten the crimp thus the strength and stiffness of the woven cloth is less than that of unidirectional tape made from the same material. An obvious way to increase the strength is to reduce crimp by having as many of the warp and fill fibres as straight as possible. This is done in the second and third types of weave.

The second type of weave is the twill or basket weave which consists of fill yarns paired two up, two down.

The final type of weaves are a family of weaves called satin weaves. These are constructions with a minimum amount of interlacing. Fill yarns skip over a greater number of warp yarns than the two in the basket weave. The length of yarn sections between two crimped intersections is called the float. Some satin weaves are illustrated in figure 45.
Figure 45. Various satin weaves

The nomenclature used to describe the type of satin weave is 'x-harness' satin weave where \((x - 1)\) is the number of warp ends that the pick passes over before going under the xth end. The satin weaves appear differently depending on which side you view. Thus, when laying up cloth for a composite, it must be specified whether each cloth is laid warp or fill face up.

An important property of carbon fibre cloth is its drapability, that is, how well the cloth conforms to being draped over complex or highly curved surfaces. To describe this property it is useful to know the number of interlacings (binders) per unit area. Interlacings are what holds the cloth together. Figure 45 shows 5 types of satin weaves all with 8 end and 8 picks per unit length but with different numbers of interlacings per unit area. The more interlacings per unit area, the more resistance the fabric will have to drape and in-plane distortion. The 8-harness stain weave in figure 45e will have the highest drapeability of those in the figure. Plain woven cloth will have the lowest drapeability due to having the maximum interlacings per unit length.

Weaving fabrics from carbon fibres is necessarily more complex than textile weaving since they are stiff, non-ductile and have low lubricity and hence a number of precautions must be taken to prevent damage during weaving. Prior to weaving the
fibres must be coated to reduce abrasion and keep yarn in a unified bundle during weaving. This coating may be removed after weaving. Woven fabrics are then reinforced at their edges to allow handling and further processing. These edges or, 'selveges', must be removed prior to lay up.

2.11.1 Multi-directional fabrics and preforms

Two-dimensionally oriented tape or fibre reinforcements are sufficient for most aerospace and racing car applications since they endure simple mechanical loading regimes. However, carbon fibre composites are strongly anisotropic and have satisfactory mechanical properties in the two dimensions containing fabric but are matrix dominated and thus typically have strength that is an order of magnitude less in the third direction. This problem is critical for artefacts required to endure isotropic fields of stress such as rocket motors. Excessive loading in the unreinforced direction results in delamination at loads less than the structure has been designed for. The solution to this problem is to add fibre reinforcements in the third direction such that the composite is reinforced in x, y and z directions. The advantages of multi-directional carbon-carbon composites is the ability to select the types and amounts of fibres in each direction to cope with a specific calculated loading system. The disadvantages are that the production costs are high, the sizes of preforms are limited by equipment and matrix impregnation between fibres in a three-dimensional array is difficult.

The simplest type of multi-directional preform is a three directional, orthogonal construction used to make rectangular blocks. Bundles of straight yarns (to preserve maximum structural capability) are located on the Cartesian co-ordinates. Such preforms are described by yarn type, number of yarns per site, spacings between adjacent sites, volume fraction of yarn in each direction and preform density.

Still more isotropic preforms are achieved by introducing yarns in additional directions. Preforms with up to 11 directions of fibre are currently produced. Preforms are described as n-D preforms where n is the number of directions and D stands for direction (not dimensions).
It is possible to form cylinders and other curved shapes using polar weaving which consists of fibres oriented on the polar co-ordinates: radial, axial and circumferential. Such preforms usually contain 50 vol.% of fibre. The weaves may be balanced (equal amounts of fibre in each direction) or unbalanced by introducing more fibres in the direction that requires most reinforcement at the expense of the other two directions. Currently, wall thickness of such shapes range from 6.4-200 mm, lengths are up to 1.3 m and diameter of 2.1 m. There is a minimum inside diameter due to the weaving apparatus requiring some space.

It is also possible to make multi-layer fabrics which may have up to 8 layers of fabric held together by warp yarns travelling from one layer to another (figure 46a). Extra in-plane ‘stuffer yarns’ may be added to increase in-plane strength (figure 46b).

![Multi-layer fabric made (a) without and (b) with stuffer yarns.](image)

Figure 46. Multi-layer fabric made (a) without and (b) with stuffer yarns.
Layers of fabric stitched together and needled felt may be considered to be 3-D preforms but have negligible strength in the inter-ply direction such that they are no improvement on 2-D preforms. The majority of multi-directional preforms are the orthogonal or polar constructions.

Infiltration or impregnation of 3-D preforms is increasingly difficult with thickness and complexity. CVD may be used on thin preforms. Thicker preforms require either vacuum impregnation followed by pyrolysis or the more effective method of hot isostatic pressure impregnation carbonisation with coal-tar or petroleum pitch as precursor matrices.
2.12 Composite Materials

There is a constant quest to improve the performance of engineering materials, usually in order to reduce weight, increase mechanical properties and reduce cost. Traditional materials are always being improved and new materials being developed. One family of relatively new materials are composite materials. The definition of a composite is a material having two or more distinct phases or constituents. To be considered as a proper composite a material must also follow three more criteria [113]. Firstly both constituents must be present in proportions of at least 5%. Secondly the properties of the composite must be different to the properties of the individual constituents and so the properties of the two constituents must be different from each other. These two criteria exclude some materials from being classified as composites which may have been thought to be composite materials. For example, plastics might have been thought to be composites because they contain additives such as lubricants and UV absorbers, but these additives are only present in very small proportions and do not change the properties of the plastic drastically and so plastics are not true composites. The third criterion for a man-made composite is that it must be produced by intimately mixing and combining the constituents.

Composites have been in use for thousands of years. Old civilisations used mud reinforced with straw to make bricks. There also exist many natural composites such as wood, bones and teeth. Materials in everyday use such as concrete are composite materials.

The two constituents of a composite must be defined. The constituent that is continuous and usually (but not always) present in greater quantity is defined to be the 'matrix'. Usually the properties of the matrix are improved by the other constituent. The three main categories of matrix used in composites are ceramics, metals and polymers. Polymers have the lowest strengths and moduli. Metallic matrices have intermediate strengths and moduli and good ductility. Ceramics are the strongest and stiffest type but also the most brittle.

The second constituent is called the 'reinforcing phase' or 'reinforcement' since it generally reinforces or enhances the mechanical properties of the matrix. The reinforcement is often harder, stronger and stiffer than the matrix. Usually, at least
one dimension of the reinforcing phase is less than 500 μm and may even be as small as 1μm. The shape and dimensions of the reinforcement are major factors in determining the physical properties of the composite. The reinforcement may be particulate or fibrous. Composites are often classified in terms of whether the reinforcement is particulate or fibrous. Figure 47, below, is one such classification scheme for composites.

![Classification of composite materials](image)

**Figure 47. Classification of composite materials**

Particulate reinforcements have a low ratio of length to cross-sectional area ("aspect ratio"). They may be spherical, cubic, platelet or other geometries. Particle reinforcements may be subdivided (figure 47) according to whether their arrangement within the matrix is random or has preferred orientation. The most common type have random orientation.

Fibrous reinforcements always have a length much greater than the cross sectional area dimension however the aspect ratio may vary greatly between reinforcements. Reinforcements with high aspect ratios are defined as continuous fibres and those with low aspect ratios are discontinuous, or chopped fibres.

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A discontinuous fibre composite has properties that vary with the length of the fibre whereas if the fibre is so long that any further increases in length does not affect the properties of the composite then the fibre is a continuous reinforcement.

Fibrous reinforcements may be made into one of many types of composite as shown in figure 47. Continuous fibre reinforcements may be used to reinforce composites in one direction only giving unidirectional reinforcement or may be woven into cloth to give two-directional reinforcements in composites. Continuous fibres may also be combined in three or more directions to make multi-directional reinforcements. Types of fibre cloths and preforms have been discussed in detail in the section on carbon fibres.

A further type of continuous fibre reinforcements are multi-layered composites. The first type of multi-layered composites are laminates which are made from layering up sheets of fibres that maybe unidirectional or two-directional woven fabrics. The layers may be stacked with their orientations the same in each layer or different in each layer. The second type of multi-layered composites are hybrids which are made from layering up sheets of reinforcement that have at least two different types of reinforcement either within each layer or layer by layer. The reinforcements may be different in that they are different materials for example glass fibres mixed in with carbon fibres or they maybe different in that some are fibrous and some are particulate reinforcements. Examples of various types of composites are shown in figure 48 [114].
It has already been described how fibres have much improved strengths and stiffnesses compared to their corresponding bulk materials. The main reason for these improved mechanical properties is that fibres have small diameters and so the average size of flaw is small. Since failure initiates at the largest flaw it follows that fibres have increased strengths. Fibre strengths and moduli may also be increased by preferred molecular orientation along the fibre axis as in aramid fibres or preferred crystallite orientation along the fibre axis as in carbon fibres. Such anisotropic fibres exhibit much improved stiffnesses and perhaps strengths compared with isotropic fibres.

It might be suggested that many fibres could be bonded together to produce a bulk substance with improved mechanical properties. The problem with this is that such a material would be very brittle as are the individual fibres. Also, the failure stress would vary greatly between nominally identical specimens due to differing surface flaws. It might also be suggested that fibres could be entwined into rope-like structures. The problems with this are that the shape of the material is then restricted and also surface damage will be incurred on the fibres. Thus we come to the principle of a matrix that holds the fibres together in a composite but holds the fibres apart from each other so that their surfaces are protected from abrasion and handling. The

Figure 48. Examples of composites. (a) particulate, random; (b) discontinuous fibres, unidirectional; (c) discontinuous fibres, random; (d) continuous fibres, unidirectional
matrix and fibres are bonded together and so loads applied to the composite are carried by both components. However the reinforcement is usually stronger and stiffer and thus bears more load than the matrix. The matrix is said to transfer the load to the reinforcement. Section 2.18 goes into detail on the principles behind the strength and moduli of composites. Figure 49(a) and (b) [115] illustrates the fact that the strengths and moduli of a number of fibre reinforced epoxy composites are much larger than those of traditional engineering materials, aluminium and steel. Figures 49(a) and (b) are for unidirectional and quasi-isotropic composites respectively.
Figure 49. Specific tensile strength versus specific tensile modulus for various commercially available 65 vol% epoxy matrix composite and for steel and aluminium. (a) Unidirectional composites; (b) Quasi-isotropic composites.
These values have been calculated from the intrinsic values of modulus and strength of the fibres as taken from the manufacturers' literature. They give good estimates for modulus values but the strengths may be incorrect by up to a factor of two or more. In spite of the approximate nature of the strength values it can be seen that both strength and modulus of composite materials are much better than conventional structural materials.

The most common type of composite in use today are glass fibre reinforced organic matrix composites which find application in industry, aerospace and military markets. The second most widely used composites are carbon fibre reinforced resin matrix composites as are discussed in the next section. Composites reinforced with aramid, other organics, boron, silicon-carbide, alumina and other ceramic fibres are also used [115-118].

In this thesis, a particular type of composite, developed for a niche in the aerospace industry will be considered: The carbon-carbon composite. These composites are composed of carbon fibres as the reinforcement phase and a carbon matrix and are the subject of the next section.
2.12.1 Carbon-carbon composites

Carbon-carbon composites consist of carbon reinforcements embedded in a carbonaceous matrix. There are two types of carbon-carbon composite: particulate composites and fibrous composites as will be described in next two sections.

2.12.2 Particulate carbon-carbon composites

The first type of carbon-carbon composites to be produced were particulate filled composites in which a carbon filler bonded to a liquid organic matrix precursor, called the binder. The filler is usually a graphitisable coke produced via the pyrolysis of a liquid phase and the binder is either a resin or a pitch. After the filler has been mixed with the binder precursor the composite is carbonised at temperatures up to 1000°C and may be graphitised up to 2500-3000°C. A wide range of particulate composites are available due to different size filler particles, different types of filler and binder, binder content and heat treatment temperature. Figure 50 [1] shows a general microstructure for this family of materials.

![Figure 50. Schematic representation of the microstructure of particulate carbon composites [1].](image-url)
They are often porous due to porosity in the original filler, porosity due to shrinkage of the binder during carbonisation and inefficient impregnation by the binder. The properties of particulate carbon-carbon composites are listed in table 8 below.

Table 8. The range of properties of particulate carbon composites

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength</td>
<td>10-120 MPa</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>up to ≈ 14 GPa</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>$10^{-6}$-$10^{-4}$ Ωm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.05-0.4 Wm$^{-1}$K$^{-1}$</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (CTE)</td>
<td>1-10×$10^{-6}$ K$^{-1}$ (dependent on structure)</td>
</tr>
</tbody>
</table>

The advantageous properties of such materials include high electrical and thermal conductivities and high thermal shock resistance. Particulate carbon-carbon composites have many applications for example as carbon electrodes, graphite electrodes and nuclear graphites as moderators. Disadvantages of these materials include their brittleness, low strength, flaw sensitivity, variable properties, isotropy and difficulties in fabricating large composites.

2.12.3 Fibrous carbon-carbon composites

These composites consist of carbon fibres in carbonaceous matrix. They were first developed in the late 1950's along with the advent of carbon fibre technology and emerged in the late 1960's as a major new genre of engineering materials [118,119]. During the 1970's they were being used in the USA and Europe for military purposes [120-125].

These materials combine the advantages of fibre reinforced composites such as strength, stiffness and in-plane toughness with the advantageous properties of carbon. These include chemical inertness and thus corrosion resistance, low density (compared to metals) and very high refractory properties in non-oxidising atmospheres. Some carbon-carbon composites retain their mechanical properties up
to and above 2000°C, well beyond the melting points of ceramics which are well known for their refractory properties. In fact the mechanical properties of most carbons improve somewhat above 2000°C. This is particularly true of fibres, probably due to improved carbon mobility at these temperatures allowing flaws to heal. Carbon-carbon composites have the best retention of mechanical properties at high temperatures of all materials as illustrated for strength in figure 51 [1].

![Graph](image)

**Figure 51.** Strength to density ratio for different classes of high temperature materials with respect to temperature [1].
Carbon-carbon composites have high thermal stabilities, high thermal conductivities and hence high thermal shock resistance and low thermal expansions. These are all properties that graphite also exhibits. The advantage the carbon-carbon composites have over graphite is their increased mechanical properties.

Different types of carbon also have varying properties that may be chosen according to the requirements of the composite. Carbons may be strong, stiff and hard or ductile and soft. They may have high porosity and large surface area or be impervious to liquids and gases. Finally, some carbon materials are brittle and others may have completely different fracture properties. This variety of properties occurs due to a variety of structural characteristics including different crystalline orders, proportions and geometries.

It is possible to produce a wide variety of carbon-carbon composites due to the many types of carbon fibres, carbon fibre cloth and preform as discussed in the section on carbon fibres. There is also a wide variety of matrix precursors that may be used such as resins that form glassy carbon matrices, pitches that produce anisotropic carbon matrices and even gases that deposit carbon as a matrix (section 2.16 on gas phase impregnation). The different heat treatment temperatures used during carbonisation and graphitisation also cause the materials to have varying properties.

There are three main disadvantages of fibrous carbon-carbon composites. The first is the cost to produce them. This is largely due to the many impregnation steps required to densify the composites. The second main disadvantage is the ease of oxidation of these carbon materials and the third disadvantage is the poor mechanical properties of the matrices. It is therefore necessary to develop “materials systems” that combine the basic composite with a number of other compounds that meet all the requirements of the material.

Applications of carbon-carbon composites include rocket nozzles and re-entry parts, aircraft brakes and racing car brakes. These applications all make use of the high refractory properties. The composites are also used as medical prostheses due to their chemical inertness and biocompatibility combined with their strength.
2.13 Fabrication of Carbon-Carbon Composites

In general the fabrication of carbon-carbon composites is a four stage process illustrated in figure 52 below.

Figure 52. The stages of fabrication of carbon-carbon composites for three types of impregnant.
Steps (1)-(4) are described here.

(1) The fibre preform is impregnated with liquid or gas phase impregnant. Suitable materials are thermosetting resins e.g. phenolic or furan based resins or thermoplastic substances including coal-tar pitch or petroleum pitch or gas phase impregnants such as hydrocarbon gases. The basic shape is formed either by the shape of the preform or by building up layers of fibre to form the shape. If the preform is gas-phase impregnated step (1) may have to be repeated several times as carbon is deposited preferentially on the outside surfaces. These outer crusts must be machined off before repeating the impregnation.

(2) The impregnated structure is carbonised at temperatures up to about 1200°C to form a porous carbon structure.

(3) (i) If the composite has been made by liquid phase impregnation the composite is re-impregnated and re-carbonised to fill in the pores and density the structure. This step needs repeating four to six times. (ii) If the composite has been gas phase-impregnated this step is unnecessary as step (1) will have been repeated enough times to densify the composite.

(4) The densified composite may be graphitised by heating to temperatures up to 3000°C. In some cases intermediate graphitisation is required.

For composites made with thermosetting resins an additional step, (1a), between steps (1) and (2) is required. This step involves curing the impregnated preform prior to carbonisation. This thermosts the resin, bonding the resin to the fibres and creating permanent cross links within the resin itself.
2.13.1 Liquid phase impregnation

As has been discussed in section 2.4 there are two types of materials that maybe impregnated in liquid phase into carbon fibre preforms to form carbon-carbon composites. The first type are thermoplastic materials such as petroleum or coal tar pitches and the second type are thermosetting materials such as phenolic or furan based resins. These two types of liquid impregnant involve different methods of impregnation due to their different properties.

2.14 Impregnation of Thermosetting Matrices

Phenolic and furan based resins will irreversibly harden or ‘thermoset’ at temperatures lower than carbonisation temperatures. The resins cure by cross linking at temperatures ranging between room temperature and 200°C. Impregnation technology that has been developed previously for other polymer matrix composites may be applied to carbon-carbon composites with thermosetting matrix precursors. There are several different methods that may be used to impregnate the fibres and form the required composite shape which are described below. After impregnation the composite is cured prior to the first carbonisation step.

2.14.1 Hand lay up

This is the simplest method of making composites and simply involves laying the fibres onto the mould by hand. In between each layer the resin is painted or sprayed on. Fibre preforms may be mats of short fibres or cloth made from continuous fibres. At the end of lay-up the composite may be evacuated or pressure may be applied to the composite to improve the impregnation into pores. The composite is then cured.
2.14.2 Pultrusion

Fibres are impregnated with the liquid resin and then pulled through a die with the required cross sectional shape such as I or T or hollow cross sections. The die may be heated to promote curing.

2.14.3 Filament winding

This method is used to make tubes and other polar shapes such as cones. Tows of unidirectional fibres are wound onto a rotating mandrel of the required shape. The mandrel may be stationary or rotating. The fibres may have been impregnated and dried prior to winding and are 'dry-wound' or may be impregnated immediately before winding by dipping in a solution containing the resin in which case the method is 'wet-winding'. There are two ways by which the fibres may be wound onto the mandrel. The first is called polar winding, where fibres are wound with no spaces between and no cross overs. The second is helical winding where there are spaces and cross overs. Both methods involve winding the fibres onto the mandrel in a helical pattern with a fixed helix angle.

2.14.4 Compression moulding

In this method fibres are pre-impregnated with resin and then pultruded through a circular die. The thin cylinder emerging is then chopped into short 'match sticks' of about 50mm in length. These short lengths are then packed into a metal press mould and cured under pressure.

2.14.5 Pre-impregnation technology

Another technology that maybe used for carbon-carbon composites made with thermosetting matrix precursors is pre-impregnation. This involves impregnating a tape of aligned fibres or a woven cloth and then partially curing the material to a
fixed degree of tackiness. The fibre preform is said to have been cured to ‘B-stage’ and is known as a ‘prepreg’. The prepreg may be used immediately or stored under refrigeration for 6-12 months. During storage, transportation and handling sheets are placed between prepregs to prevent them sticking together. These prepregs may be formed into the required shapes using any of the above methods or thin sheet prepregs may be layered up to form laminates. Laminates may be laid up unidirectionally (figure 53(a)) in which case the resulting composite will have high strength and modulus in the reinforced direction only. They may be laid up as a with 0°/90° layers (figure 53(b)) in which the transverse properties are improved at the expense of the axial properties. Other lay-ups include layers orientated at various angles are produced to increase strength and modulus in required directions. A 0°/90°±45° lay-up (figure 53(c)) approaches isotropic in-plane behaviour asymptotically with increasing thickness and is thus known as a ‘quasi-isotropic’ laminate. Once the prepreg is in its required form it is fully cured by compression moulding or autoclaving (heating in a pressurised vessel). Curing causes the resin impregnant to thermoset fully and bond with the fibre preform. In the case of laminates curing bonds the layers together. Finally the cured composites are carbonised.
Figure 53. The most commonly used lay-ups of unidirectional prepregs.
2.15 Impregnation of Thermoplastic Matrices

On heating a typical pitch becomes a liquid with low viscosity between 240-260°C [126]. No further significant increase in viscosity occurs until around 475°C and thus a temperature of around 240-260°C is used for impregnation.

The techniques described above for thermosetting matrices are not applicable to thermoplastic ones. The matrix precursor, usually pitch, does not set permanently below temperatures of carbonisation and so during carbonisation the pitch becomes plastic again. The matrix will not remain in a shape it may have been set in. The matrix will run out of the composite and will also cause bloating of the composite due to release of volatiles that occurs throughout its plastic state. Any method making composites with a thermoplastic matrix precursor must somehow maintain the composite in the required shape during carbonisation and prevent run-out and bloating. There are two methods that prevent these things occurring to certain extents: hot isostatic pressure impregnation carbonisation and oxidation of the matrix precursor. These methods are described in the next two sections.

2.15.1 Hot isostatic pressure impregnation carbonisation (HIPIC)

This method uses the simple principle that application of pressure to the impregnated composite during melting and carbonisation will prevent the matrix from leaking out of the composite.

First the dry fibre preform is placed in a metal container. The preform is then conventionally vacuum-impregnated with molten pitch. The metal container is then re-filled with an excess of pitch and then evacuated and sealed. The fourth stage is the HIPIC. The apparatus for HIPIC consists of a furnace surrounded with insulation material (the 'thermal barrier') and sealed in a water cooled pressure vessel. The pressure in the vessel is created by use of inert gas.

A pressure differential is set up between the pressure vessel inner wall (at a over pressure of around 1.5 bar) and the work zone (at a lower pressure). The two zones are separated by the isolation hood. This means that all the hot gases are
isolated in the work zone and any movement of gases is inwards. The temperature in
the work zone is raised at a programmed rate above the melt point of the pitch. The
pitch melts and is forced by the pressure differential into the pores in the sample. The
sealed container transfers the pressure to the sample. As the temperature increases the
pitch and fibres begin to carbonise. The pressure is increased to around 100MPa. The
pressure prevents the gaseous pyrolysis products forcing the molten pitch out of the
pores. The fifth and final stage of the HIPIC stage is to remove excess carbonised
liquid from the surface of the sample. The complete cycle of these stages of HIPIC
must be repeated until the required density has been reached.

As well as preventing run-out and bloating, another advantage of using the
HIPIC method is that the application of pressure increases the carbon yield. Carbon
yields increase from about 50% at atmospheric pressure to 90% with the application
of a pressure of 100MPa [127]. The reason for the increased carbon yield is that under
pressure the volatiles remain in a condensed phase within the work zone and may
carbonise thus increasing the carbon yield of the composite. This obviously reduces
the need for as many densification cycles. Figure 54 [128] shows the effect of
pressure on carbon yield.
Figure 54. Effect of carbonisation pressure on carbon yield from petroleum pitch.

It has also been shown that application of pressure affects the matrix microstructure. Figure 55 [129] shows micrographs of petroleum pitch carbonised at 6.89 and 68.9 MPa respectively. The coke formed at lower pressure is needle-like due to the percolation of gas bubbles through the mesophase. The coke formed at higher pressure has a more coarse, isotropic structure due to less volatiles escaping from the matrix.
It has been shown that increased pressures lower the temperature at which mesophase is formed so not only are fewer volatiles escaping but fewer are being formed. At very high pressure of around 200MPa mesophase does not coalesce at all and so an optimum of 100MPa is chosen for HIPIC [130].

A disadvantage of HIPIC is the size limitation due to the size of the HIPIC unit.

### 2.15.2 Oxidation of the matrix precursor

White and Sheaffer [131] postulated and proved that another method of preventing bloating during carbonisation is to stabilise the matrix precursor prior to carbonisation in a similar way that oxidation of carbon fibres stabilises them during carbonisation [132]. White and Sheaffer used orthogonal 3-D fibre preforms impregnated with petroleum pitches. The samples were oxidised in oxygen for up to 100 hours at 220°C followed by carbonisation at 1100°C. It was found that the oxidation prevented bloating and, as in application of pressure, retained the mesophase spherules thus preserving the microstructure when plastic. Carbon yield is increased due to fewer volatiles being released. Further experiments conducted on 2-D preforms showed that unoxidised samples were destroyed during carbonisation whereas oxidised ones

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**Figure 55.** Microstructure of petroleum pitch carbonised under (a) 6.89 MPa and (b) 68.9 MPa applied pressure - subsequently graphitised to 2700°C.
remained intact (figure 56). This technique would remove the size limitation put on 2-D preforms using the HIPIC method.

Figure 56. The effect of prior oxidation on the carbonisation of 2-D carbon-carbon [131].
2.16 Chemical Vapour Impregnation (CVI)

In this process gaseous species are decomposed or react on the substrate carbon fibre preform to form a solid carbon matrix which nucleates and grows on the substrate. The fibre preform must be heated in a gaseous environment for the matrix to be deposited. It is possible to finely control the composition and morphology of the solid using this method of impregnation. However the rate of deposition is slow and thus a large expenditure of materials and energy is required making it a costly process.

2.16.1 Thermodynamics

At high temperatures hydrocarbon gases are thermodynamically unstable relative to carbon solid. For example, consider the decomposition of methane:

\[ CH_4(g) \rightarrow C(s) + 2H_2(g) \] (1)

There is a volume increase in the system.

The entropy for the isothermal expansion of a gas is given by

\[ \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \] (2)

Since \( \frac{V_f}{V_i} \) is greater than unity the entropy change in the system is large and positive.

The free energy of the system is given by

\[ \Delta G = \Delta H - T\Delta S \] (3)

The \( T\Delta S \) term overcomes the endothermic enthalpy term giving a negative change in free energy. Hence the reaction is thermodynamically stable and carbon is deposited on the fibre preform.
In fact methane is a very stable hydrocarbon and requires temperatures in excess of 550°C before it decomposes. Even at 550°C the rate of deposition is slow and so higher temperatures, typically 900-1100°C, are required for measurable deposition rates. Despite this, methane is still the most widely used hydrocarbon gas for CVI due to its availability and good diffusion properties. The process is usually carried out at low pressures in order to improve diffusion of the methane by increasing its mean free path. Dilutent gases such as H₂, He, N₂ or Ar may be added to modify the deposited structure.

2.16.2 Mechanism and kinetics

Spear [133] has accounted for the different processes occurring during CVI:

1. Forced flow of reactant gases into the reaction vessel
2. Diffusion of reactants through the laminar flow boundary layers around the substrate
3. Adsorption of reactants onto surface of substrate
4. Reaction of adsorbed reactants to give solid products and adsorbed gaseous products
5. Desorption of adsorbed gaseous products
6. Diffusion of gaseous products through the boundary layer region.
7. Forced flow of gaseous products through reaction vessel exit.

It has been found empirically that at low temperatures and pressures the rate determining step is the surface reaction kinetics and at high temperatures and pressures the rate determining step is the diffusion of reactants onto the substrate.

The reactions at the surface are all heterogeneous and can be complex. In the above example of methane it has been found [134] that there are a range of aromatic products suggesting that a series of dehydrogenation/polymerisation reactions are occurring to produce a graphitic matrix. If the temperature is too high, pre-reaction
occurs in the gas phase forming soot particles which are then deposited on the substrate leading to a low-density, mechanically weak carbon matrix.

It has been concluded [135] that the kinetics of the deposition are a complex function of reaction conditions including temperature, pressure, gas phase composition, gas flow rate and substrate geometry and type. Figure 57 shows the plot of rate constant versus temperature for a number of different hydrocarbon precursors.

Figure 57. Dependence of carbon deposition rates on temperature and type of hydrocarbon precursor during the CVI process. [1]

All hydrocarbons produce an Arrhenius-type dependence of rate on temperature, but rate varies according to type of hydrocarbon. It has also been shown [136] that ‘hot
wall' and 'cold wall' reaction vessels result in different types of carbon deposits at a given temperature. The hot wall system results in sooty isotropic deposits due to homogeneous gas phase pre-reactions whereas cold wall systems result in laminar deposits as gas preheating is avoided.

2.16.3 CVI in a pore system

So far only deposition on a flat surface has been considered. However, we are concerned with deposition in a fibre preform which will have a well defined pore system whether it is made from discontinuous or continuous fibres. The matrix must be deposited throughout the pore structure. This makes the CVI process much more complex. The reactants must diffuse through the boundary layer of laminar flow around the preform and into the pores where it must react, desorb and diffuse out again.

If the surface reaction occurs too rapidly with respect to diffusion then deposition will occur at the mouth of the pore and block the pore (figure 58(a)). The resulting closed porosity concentrates mechanical stress and so is detrimental to the mechanical properties of the composite. If the surface reaction rate is a much slower than the diffusion rate then deposition will occur evenly along the whole length of the pore giving a well densified material (figure 58(b)).
There are several factors that affect the rates of surface reaction and diffusion. Those affecting rate of reaction have already been discussed. Diffusion in the coarse pores in fibre preforms is probably mainly bulk diffusion, where pore size is irrelevant (as opposed to Knudsen diffusion where pore size is important due to the effect of molecule-wall collisions). Bulk diffusion rate is influenced by temperature, pressure, molecular weights and collision cross sections of molecules involved.

Diffusion kinetics and surface reaction kinetics can be combined and an expression for the ratio of reaction rate at a point along the pore to the reaction rate at the mouth of the pore can be expressed terms of a dimensionless number, the Thiele modulus, $\varphi$ where

$$\varphi = \frac{L}{2d} \left( \frac{4k}{D_e} \right)$$

where $L$ is the length of the pore, $d$ is the pore diameter, $k$ is the rate constant for the surface reaction and $D_e$ is the diffusion constant for the reactant gases.

Figure 59 is a plot of the ratio of deposition rate at a given distance from the pore mouth to the rate at the pore mouth as a function of this distance. Curves for different values of $\varphi$, which represents different reaction conditions, are shown. High values of $\varphi$, which corresponds to a high surface reaction rate compared to diffusion,
result in a high reaction rate at the pore mouth compared with further along the pore where ratio of reaction rates drops sharply. At low values of $\phi$ corresponding to slow surface reaction rates, the reaction rate is almost constant along the pore length leading to good pore filling.

![Graph showing the role of the Thiele modulus](image)

Figure 59. Theoretical deposition/pore depth profiles; the role of the Thiele modulus

Experiments have been performed [137] verifying that variation of reaction conditions lead to different deposition/length profiles. Of course, low reaction rates which are vital for good pore filling lead to long processing times. A balance must be achieved between efficient pore filling and economical process times.

2.16.4 Experimental CVI techniques

The conventional, isothermal CVI method is discussed here along with other methods that have been developed to remove the diffusion constraints on pore filling.
2.16.5 Isothermal method

Figure 60 below shows the apparatus for an isothermal CVI process.

![Diagram of isothermal CVI process](image)

**Figure 60. The isothermal method of CVI processing**

The reaction vessel is maintained at a constant temperature. The substrate is placed in the vessel and reaction gases (perhaps with a carrier gas) are passed over it. The surface reaction rate must be kept below the diffusion rate for good filling of pores. The rate of weight gain is thus very slow and process times are very long. Rate of densification also slows even more as the porosity decreases making full densification impossible. Selection of reaction parameters must be a compromise between obtaining a fully densified composite and economic considerations. Composites are usually densified for about a week and then taken out and machined to remove the surface consisting of entirely blocked pores. This process is repeated about four times so that the overall processing time is about 1 month. The isothermal process is easily scaled up and furnaces may densify more than one composite at a time.
2.16.6 Thermal gradient method

This method involves setting up a thermal gradient across the width of the fibre preform. The preform is applied to a mandrel that is a susceptor for inductive heating (usually solid graphite). The internal surface is in contact with the heated mandrel and is thus at a higher temperature than the external surface. To ensure a good temperature gradient is attained a preform with a low thermal conductivity (usually carbon felt) is chosen along with an appropriate temperature. The gas flow rate is kept high to keep the external temperature low. Temperature gradients of up to 500°C across a 1cm thick preform have been observed [138]. The idea is that deposition only occurs on the hotter internal surface initially and then matrix deposition moves outwards. Also higher rates of deposition (of up to one order of magnitude) [139] are obtainable. Other advantages of this method are the lower incidence of crusts and the ability to run at atmospheric pressure. A disadvantage, is the difficulty involved in scaling up and restriction to one preform per impregnation.

2.16.7 Pressure gradient method

In this method a fibre preform is sealed into a gas-tight unit and placed into a heated vessel. As gas enters the unit containing the preform the pressure builds up from one side of the preform to the other causing a pressure gradient. This removes the diffusion limitation as the pressure gradient increases the diffusion rate into the pores. As the process progresses the pores fill up and so pressure gradient increases and hence so does deposition. This is opposite to the decrease in deposition rate as the process progresses for the methods discussed so far.

A disadvantage is that, again, there is a limit of producing only one item at a time. Also high temperature and pressure seals are required which may be expensive. Overcrusting will occur and thus removal and machining is necessary in-between impregnations. This method is thus not in widespread commercial use.
2.16.8 Pulse CVI methods

In this method the reaction vessel is alternately under vacuum (a few torr) and at atmospheric pressure. This forces reactant gases deep into the pores thus removing the diffusion limitations. The precursors react and are then pumped out before fresh reactant gases are introduced. It has been found [140] that precise adjustments of the timing of the vacuum/gas cycles are necessary to create a reasonable deposition at each cycle. This method has not been commercially exploited due to difficulties in setting up fast pressure cycles.
2.17 Microstructure of Carbon-Carbon Composites

It has already been stated that the properties of a composite are dependant on the microstructure of the composite. The microstructure includes the volume fractions of both of the reinforcement and the matrix and their individual microstructures. The properties of the reinforcement that describe its microstructure are the architecture in terms of orientation and distribution along with shape and size. The type of fibre, which may be HS or HM and may be derived from a number of different precursors such as rayon, PAN or pitch obviously has an effect on the composite microstructure. Microstructures of carbon fibres have been discussed in section 2.8.

There are various properties of the matrix that describe its microstructure including grain size for polycrystalline matrices as in carbon-carbons. Whether a thermosetting resin, a thermoplastic pitch or CVI matrix or a combination of these is used obviously affects the microstructure of the composite.

The microstructure of carbon-carbons also includes the properties of the interface between matrix and fibre including the strength of the interfacial bonds. The pore and crack structure of the composite also makes up its microstructure. The microstructures of carbon-carbon composites have been reviewed by both Savage [1] and Murdie et. Al. [141]. Microstructures of composites with the three different types of matrix will now be considered.

2.17.1 Microstructure of CVI-matrix composites

There are three types of possible microstructures resulting from CVI impregnated composites: isotropic, rough laminar and smooth laminar. Isotropic structures may be truly amorphous or consist of very small domains of graphitic carbon, a few micrometers in size, randomly orientated throughout the composite. Smooth laminar microstructures consist of carbon layers with weak anisotropy that surround the fibres. Rough laminar microstructures consist of layers that are highly anisotropic and surround the fibres uniformly. All three microstructures are illustrated in figure 61.
Figure 61. CVD-derived carbon microstructures: (a) rough laminar; (b) smooth laminar; (c) isotropic. [1]

The factors which determine which of the three types of microstructure is obtained are the processing temperature, concentrations of reactant gases, amount of added H₂ and ratio of the decomposition products of methane, [C₂H₂]:[C₆H₆]. The conditions for the three types of microstructure are summarised in table 9 below [142].
Table 9. Factors affecting the type of microstructure of carbon-carbon composites

<table>
<thead>
<tr>
<th>Microstructure Type</th>
<th>Deposition Temperature</th>
<th>Partial Pressure</th>
<th>Amount of added $\text{H}_2$</th>
<th>Ratio of methane decomposition products, $[\text{C}_2\text{H}_2]:[\text{C}_3\text{H}_6]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth Laminar</td>
<td>low</td>
<td>high</td>
<td>none</td>
<td>$&lt;5$</td>
</tr>
<tr>
<td>Rough Laminar</td>
<td>intermediate</td>
<td>intermediate</td>
<td>some</td>
<td>$&gt;5$, $&lt;20$</td>
</tr>
<tr>
<td>Isotropic</td>
<td>high</td>
<td>low</td>
<td>large amount</td>
<td>$&gt;20$</td>
</tr>
</tbody>
</table>

However CVI composites obtained under the same temperature and pressure may have different morphologies. CVI composites may also consist of a combination of the three types of structure. For example figure 62 [143] is an optical micrograph of graphitised CVI-matrix, PAN-fibre composite. Immediately adjacent to the fibre surface is an isotropic phase and a bit further out from the fibre is a second, highly oriented phase with layers parallel to the fibre surface.

Figure 62. Optical micrograph of closed porosity in PAN-CVI carbon-carbon composite
It has been shown that the bonding between isotropic CVI matrices and fibres is stronger than the bonding between lamellar CVI matrices and fibres. Figure 63 is a dark field TEM micrograph of the composite in figure 62.

![TEM dark field image of CVI deposit on PAN fibre showing gradual transition from grainy isotropic to laminar structure.](image)

**Figure 63. TEM dark field image of CVI deposit on PAN fibre showing gradual transition from grainy isotropic to laminar structure.**

It shows the gradation from fibre to isotropic CVI matrix to a lamellar CVI matrix. The interface between fibres and the matrix has no cracks in it. The cracks that can be seen are in the lamellar matrix that is further away from the fibre-matrix interface. Compare this to figure 64 which is an SEM of a CVI composite which has been processed under conditions such that no isotropic layer is deposited adjacent to the fibre surface and only lamellar matrix structures are present.
Figure 64. SEM micrograph of pitch/CVI composite (atomic oxygen etched)

The interface between fibre and matrix in this figure is cracked. Since both specimens were subjected to similar process conditions it can be concluded that the bonding between isotropic CVI matrices and fibres is stronger than the bonding between lamellar CVI matrices and fibres. In most cases the type of fibre used does not affect the interfacial bond as much as the type of matrix that is deposited.

In terms of pore structure, CVI matrices have few small pores as these are filled well using CVI but there are more large pores as CVI is inefficient at filling such pores. Figure 65 is a higher magnification of the same sample as in figure 62. It shows a large closed pore typical of CVI composites. Figure 63 shows that the lamellar CVI deposits contain slit shaped microfissures that are <1 μm in length and <0.1 μm in width whereas the isotropic CVI deposits contain no cracks. This is generally true.
2.17.2 Microstructure of pitch-matrix composites

The microstructure of pitch-matrix composites pyrolysed at ambient pressures consists of highly graphitic planes. The graphitic planes are orientated parallel to the fibre axis at the fibre-matrix interface and become more and more random with increasing distance from the fibre as illustrated schematically in figure 66 [144].

Figure 65. Optical micrograph of closed porosity in PAN-CVI carbon-carbon composite (graphitised).

Figure 66. Matrix alignment in fibre-reinforced pitch composites.
This is the opposite to the situation for CVI matrices which have isotropic structures nearest to the fibre turning into more graphitic layers further from the fibre. Figure 67 is an SEM of a pitch-matrix composite etched with atomic oxygen. The intrabundle matrix planes (i.e. very close to the fibres) are parallel to the fibre surface.

Figure 67. SEM micrograph of transverse section of a fibre bundle showing fibre/intrabundle matrix interface after etching with atomic oxygen at 100°C for 3 hours.

The alignment with the fibre surface only exist for a distance of between $2\mu m$ and a maximum of about $6\mu m$ before becoming more random [145]. The reason that the graphitic layers align parallel to the fibre is that during the mesophase state of the pitch the discotic liquid crystals that become the layer planes can easily shear past one another. The liquid crystals will thus preferentially orientate themselves parallel to any surface across which they move i.e. the fibre surface.

The matrix may consist of aligned graphitic planes and these may have non-uniform optical textures. Figure 68 is an optical micrograph of a 3-D CC composite composed of PAN fibres and a coal tar pitch matrix. At position A a transversely orientated fibre bundle may be seen. Surrounding this, at position C, is the interbundle matrix. The matrix consists of some coarse-grain mosaics and some fine-
grained mosaics. The variation in optical texture causes different mechanical properties and chemical reactivities [146,147].

![Photomicrograph of a PAN/coal tar pitch carbon-carbon composite](image)

**Figure 68. Photomicrograph of a PAN/coal tar pitch carbon-carbon composite**

The bonding between layers in the matrix are weaker than those between pitch and fibre. This is illustrated in figure 69 which is an SEM of a single fibre from the same sample as figure 67. There are two fissures in the matrix at some distance from the fibre but none at the fibre-matrix interface hence the fibre-matrix bond is stronger than the intramatrix bonds.
At higher magnifications as in figure 70 some fissures can be seen at the interface showing that the interface is not actually continuous. The fissures are smaller at smaller distances from the fibre. This is opposite to thermoset resin-matrix composites where the matrix shrinks away from the fibres. It has been seen from lattice fringes that the crystallite size in the pitch matrix can be up to 10 times larger than those in a PAN fibre.
Figure 70. Photomicrograph of the interface between PAN fibre and pitch matrix

The pore structure at ambient pressures is mainly open porosity with a variety of geometries. There are two main types of pore that are both illustrated in figure 68. Position D shows a large void that has resulted from escape of volatiles during pyrolysis and position E shows a crack or fissure formed due to shrinkage of the matrix during cool down.

At increased pressures carbon yield increases due to suppression of mesophase formation. As a result of the suppression of mesophase more isotropic microstructures occur. Above 30 MPa the structure is completely isotropic except very close to the fibres [139]. Some studies have found that increased pressure favours transverse alignment of graphitic planes [148]. The pore structure at increased pressures consists of many closed pores that are mainly spherical and of uniform size distribution.

Oxidation and addition of sulphur are also used to increase carbon yields. The effect of such treatments is to cause cross-links to form in the pitch. There is less loss of volatiles as a result, and the pitch is said to have 'pseudo-thermoset'. This causes the microstructure to be glassy as in thermoset resin-matrix composites.
2.17.3 Microstructure of resin-matrix composites

When thermosetting resins are carbonised alone, their bulk structure is a glassy isotropic carbon with no graphitic regions. They are optically isotropic and have low porosity and permeability. When present in a composite prior to carbonisation the resin, again, has a glassy, isotropic structure as illustrated in figure 71.

Figure 71. Photomicrograph of a moulded pitch fibre in phenolic resin (hot pressed)

However after carbonisation at temperatures above 1000°C some graphitic regions near the fibre-matrix interface are formed. Hence the microstructure of composites with thermosetting resin matrices varies a lot according to the heat treatment temperature used. Figure 72 shows a carbonised resin-matrix composite. Some intrabundle matrix regions are optically anisotropic but this anisotropy is restricted to regions within <2μm of the fibre.
The degree of preferred orientation depends on the resin type and process conditions. For example, furan-based resin matrix-precerursors exhibit a lot of graphitic regions near the interface, even at temperatures below 1000°C. Figure 73 is an optical micrograph of a furfural alcohol resin-matrix composite. The intrabundle matrix regions exhibit a high degree of alignment of basal planes parallel to the fibre surface and interbundle matrix regions also show a high degree of alignment parallel to the fibre bundle/matrix boundary (position F).
If furan is heated to temperatures in excess of 2200°C then the anisotropic domains change into graphite. At temperatures above 2800°C the matrix is completely graphitic. As in pitch-matrix composites the graphitic planes encircle the fibres as can be seen in figure 74 which is a transverse SEM of a graphitised resin-matrix composite that has been etched using acid. The graphite layers envelope the fibre. Phenolic resins, in comparison to furan resins, are more difficult to orientate.
Figure 74. SEM of a graphitised carbon-carbon composite, acid etched to show the lamellar structure of the matrix in the vicinity of the fibre/matrix interface.

The graphitisation of non-graphitising carbons is due to high stresses between fibre and matrix due to thermal expansion mismatch at high temperatures. This is called "stress graphitisation" [149,150].

The mechanism of stress graphitisation is poorly understood but a number of studies have been done[151-153].
The rate of stress graphitisation and temperature at which it occurs depends on the type of fibre use. For example HM fibres have a lower temperature and faster rate of stress graphitisation.

The porosity of the resin-matrix composites before carbonisation is low (less than 3%) and density is about 1.5 g/cm³ (figure 71). However, the porosity of resin-matrix composites after carbonisation is quite extensive. During carbonisation pores are formed as a result of volatilisation of smaller molecules and the resin shrinks extensively leading to a porosity of 30-40% and bulk density of 1.2-1.4 g/cm³ (figure 72). Shrinkage occurs away from the fibres suggesting that the bond between fibre and resin-matrices are relatively weak. Shrinkage has been so excessive that the resin has shrunk away from almost all of the fibres in this region. Temperatures above 2000°C results in significant shrinkage as a graphitic structure is formed. This is why intermediate graphitisation cycles may be used to increase access to porosity for subsequent impregnation cycles. Figure 75 is a polarised light micrograph of a thermoset-matrix, intermediate modulus fibre composite. After the first carbonisation cycle the composite was graphitised to open up porosity and then reimpregnated / recarbonised four times with a mixture of pitch and furan resin. The composite is still not fully densified.

![Figure 75. Polarised optical micrograph of densified composite showing optical anisotropy resulting from graphitisation and lined but open microcracks and pores illustrating inefficient re-impregnation](image)

141
Figure 76 is a matrix-rich region of the same composite. The bottom left hand corner shows clear optical anisotropy which grades into isotropic matrix as distance from the fibre increases. It can thus be concluded that the microstructure is strongly affected by the presence of fibres and associated thermal stresses.

Figure 76. Polarised light micrograph illustrating stress graphitisation in phenolic-based matrix

To reduce the shrinkage of the resin matrix and increase the carbon yield, fillers, such as carbon black, may be added to the matrix. Figure 77 is a TEM of a phenolic-resin matrix doped with carbon black. As well as restricting shrinkage and increasing carbon yield the carbon black particles act as nuclei for the growth of anisotropic regions (positions D and G). In some areas preferred orientation still does not develop (position H). Microcracks form between basal planes of the aligned matrix, concentric to the carbon black particles. These microcracks presumably contribute to the reduction in apparent shrinkage of the resin.
Figure 77. Bright field image of graphitised phenolic resin containing carbon-black particles.
2.18 Composite Theory

2.18.1 Law of mixtures and property-determining parameters

Consider the simple case of a tensile load applied to a unidirectional composite (the load is applied parallel to the fibre axes). The applied load is shared between the individual components of the composite:

\[ L_c = L_m + L_f \quad (1) \]

where \( L \) refers to the load and subscripts \( c, m \) and \( f \) refer to composite, matrix and fibre respectively.

If \( A \) is the cross sectional area and \( \sigma \) is the applied stress then:

\[ \sigma = \frac{L}{A} \quad (2) \]

Combining equations (1) and (2) to give:

\[ \sigma_c A_c = \sigma_m A_m + \sigma_f A_f \quad (3) \]

If the cross sectional area of matrix and fibres is equal along the entire length of the composite then area terms may be substituted by volume fraction terms. Volume fractions may be written in terms of areas:

\[ V_m = \frac{A_m}{A_c} \quad V_f = \frac{A_f}{A_c} \quad (4) \]

where \( V_m + V_f = 1 \)

Substituting equations (4) into equation (3) and dividing by \( A_c \) gives:
\[ \sigma_c = \sigma_m V_m + \sigma_f V_f \quad (5) \]

This is the law of mixtures. This equation does not only apply to the stress on the composite but to other properties of composites. A generalised form of the equation is

\[ X_c = X_m V_m + X_f V_f \quad (6) \]

where \( X_c \) represents an appropriate property of the composite and, as before, \( V \) is the volume fraction where subscripts \( c, m \) and \( f \) refer to composite, matrix and fibre respectively.

Most properties of a composite are a complex function of a number of parameters as the matrix and fibre interact so that properties of the composite are not fully accounted for by the law of mixtures. The chemical strength of the interface between matrix and fibres is particularly important in determining the properties of the composite. The interfacial bond strength must be sufficient for the load to be transferred to the fibres from the matrix if the composite is to be stronger than the unreinforced matrix but the interface must not be so strong that it does not fail and allow toughening mechanisms that prevent crack propagation to take place (such as debonding and fibre pull-out).

Other parameters that may affect the properties of the composite are the shape, size, orientation and distribution of the reinforcement and various properties of the matrix such as grain size for polycrystalline matrices. These factors, along with the volume fraction of the fibres and matrix all constitute the microstructure of the composite.

However, even for properties which are dependent on microstructure and do not obey the law of mixture, the volume fractions still play a major role in determining properties. The volume fraction is the single most important parameter influencing the composite properties. It is easy to vary this factor and hence control the properties of the composite.
2.18.2 Tensile strength and modulus of composite materials

In the following discussion we use the law of mixtures to be correct to a first approximation and we consider three cases where the relative strains of matrix and fibre are in different proportions. In each case we derive equations for the tensile strength and modulus of the composite using a number of approximations along the way.

CASE A: Matrix and fibre have equal ultimate strains

\[ \varepsilon^u_m = \varepsilon^u_f \quad (7) \]

If the fibres and matrix are perfectly bonded then the principle of combined action is obeyed and the strain in the composite as a whole is equal to the strain of its components:

\[ \varepsilon_c = \varepsilon_m = \varepsilon_f \quad (8) \]

Equation (5) is differentiated with respect to strain:

\[ \frac{d\sigma_c}{d\varepsilon_c} = \frac{\partial \sigma_m}{\partial \varepsilon_m} V_m + \frac{\partial \sigma_f}{\partial \varepsilon_f} V_f \quad (9) \]

In the region that Hooke’s Law applies

\[ \frac{d\sigma_c}{d\varepsilon_c} = E_c \quad \frac{\partial \sigma_m}{\partial \varepsilon_m} = E_m \quad \frac{\partial \sigma_f}{\partial \varepsilon_f} = E_f \quad (10) \]

Substituting equations (10) into (9) gives
\[ E_c = E_m V_m + E_f V_f \quad (11) \]

where \( E \) represents Young’s Modulus

For CASE A

Equation (11) shows that the modulus of the composite is equal to the sum of the component values weighted according to their volume fraction.

Via Hooke’s law equation (11) can be converted to:

\[ \sigma^* = \sigma_m^* V_m + \sigma_f^* V_f \quad (12) \]

where \( \sigma^* \) refers to the ultimate stress i.e. the strength

Equation (12) shows that the strength of the composite is equal to the sum of the component values weighted according to their volume fraction.
CASE B: The ultimate strain taken up by the matrix is more than that taken up by the fibres

Consider the case when the ultimate strain in the fibres is much lower than the ultimate strain of the matrix:

$$\varepsilon_f^u < \varepsilon_m^u$$ (13)

The composite will fail when its longitudinal strain reaches the ultimate tensile strain in the fibre as illustrated in figure 78 [154]

![Stress-strain curve for fibre dominated strength](image)

**Figure 78. Stress-strain curve for fibre dominated strength**

where $\sigma_c^u$ is the longitudinal composite strength, $\sigma_f^u$ is the longitudinal fibre strength, $\sigma_m'$ is the average matrix stress when the ultimate fibre strain is reached, $\varepsilon_f^u$ is the ultimate fibre strain and $\varepsilon_m^u$ is the ultimate matrix strain.
The strength of such a composite is said to be a fibre dominated strength.

The longitudinal tensile strength of the composite can be approximated by:

\[ \sigma_c \approx \sigma_f V_f + \sigma_m V_m \]  (14)

Assuming linear elastic behaviour,

\[ \sigma_m' = E_m \varepsilon_f \]  (15)

Substitute (15) into (14) gives

\[ \sigma_c \approx \sigma_f V_f + E_m \varepsilon_f V_m \]
\[ = \sigma_f \left( V_f + V_m \frac{E_m}{E_f} \right) \]  (16)

For composites with very stiff fibres, \( E_f \gg E_m \), equation (16) may be further approximated by:

\[ \sigma_c \approx \sigma_f V_f \]  (17)

Using Hooke's law equation (17) may be re-written as

\[ E_c \approx E_f V_f \]  (18)

Resin and metal matrix composites have been found to have experimentally determined moduli in good agreement with those calculated using equation (18) whereas C/C composites have experimentally determined moduli that were higher than the values calculated by this equation suggesting that C/C composites include a significant contribution to stiffness by the matrix as well as the fibres [155].
CASE C: The ultimate strain taken up by the fibres is more than that taken up by the matrix

Consider the case when the ultimate strain in the matrix is much lower than the ultimate strain of the fibres:

\[ \varepsilon^u_m < \varepsilon^u_f \] (19)

The composite will fail when its longitudinal strain reaches the ultimate tensile strain in the matrix as illustrated in figure 79 [154].

---

**Figure 79. Stress-strain curve for matrix-dominated strength**
where $\sigma_e^u$ is the longitudinal composite strength, $\sigma_m^u$ is the longitudinal matrix strength, $\sigma_f'$ is the average fibre stress when the ultimate matrix strain is reached, $\varepsilon_f^u$ is the ultimate fibre strain and $\varepsilon_m^u$ is the ultimate matrix strain.

The strength of such a composite is said to be a matrix dominated strength.

The longitudinal tensile strength of the composite can be approximated by:

$$\sigma_e^u \approx \sigma_f' V_f + \sigma_m^u V_m \quad (20)$$

Assuming linear elastic behaviour,

$$\sigma_f' = E_f \varepsilon_m^u \quad (21)$$

Substitute (21) into (20) to get

$$\sigma_e^u \approx \sigma_m^u V_m + E_f \varepsilon_m^u V_f$$

$$= \sigma_m^u \left( V_f \frac{E_f}{E_m} + V_m \right) \quad (22)$$

For composites with a very stiff matrix, $E_m \gg E_f$, equation (22) may be further approximated by:

$$\sigma_e^u \approx \sigma_m^u V_m \quad (23)$$

In general a stiff matrix is one that is highly oriented and so a composite made from a pitch-based matrix precursor will have a higher matrix contribution to composite stiffness than, say a resin matrix. Indeed Fitzer and Hütter [156] found this to be the case.
Using Hooke's law equation (23) may be re-written as

\[ E_c \approx E_m V_m \quad (24) \]

In this matrix-dominated case the whole strength of the fibres is not utilised and the following shows that using weaker, HM fibres actually results in a stronger composite than using stronger, LM fibres.

Consider using stiff (HM) fibres. In this case \( E_f \gg E_m \)

This allows equation (22) to be further approximated as

\[ \sigma_{\epsilon}^{u} \approx \sigma_{m}^{u} \left( V_f \frac{E_f}{E_m} \right) \]
\[ = \epsilon_{m}^{u} E_f V_f \quad (25) \]

This equation assumes that the matrix carries no load.

It can be shown [157] that if the maximum strain of carbon matrices, \( \epsilon_{m}^{u} \), is approximately 0.3\%, then the strength of a composite containing 50 vol. % of high modulus fibre (517GPa) will be 776MPa and the strength of a composite containing 50 vol. % of low modulus fibre (206GPa) will be 309MPa. Thus the high modulus fibres result in the composite with higher strength.
2.19 Literature review summary

This review has looked at the natural allotropes of carbon and its two main synthetic forms: carbons from thermosetting and thermoplastic precursors. Coal-tar pitch as carbon precursor has specifically been studied with a view to using it as the matrix precursor for the carbon-carbon composites in this study. The use of thermosetting and thermoplastic materials as matrix precursors for carbon-carbon composites has been reviewed, including the various pre-treatments used for coal-tar pitch to improve its properties as a matrix in a carbon-carbon composite.

Specific detail on sparging coal-tar pitch has revealed that there are contradictory reports as to whether this process is a simple volatile stripping reaction or whether it involves chemical processes, and if so, what is the nature of these processes. The first part of this work was aimed at determining the nature of any chemical processes that occur during sparging with hydrogen or oxygen gases for two different pitches.

This review has considered the strength of carbon materials in order to gain a knowledge of the factors that determine the strength. This theory was later extended to the theory of the strength of composites. Carbon fibres and carbon-carbon composites were reviewed in detail. Types of raw materials and methods of fabrication were reviewed in order to devise the method used in this work to fabricate carbon-carbon composites. The manufacture of carbon-carbon composites using the coal-tar pitches fabricated in the first part of this work forms the second part of this project.

The final part of this study involved the characterisation of the composites. The characteristics were correlated to the treatments of the constituent pitches to determine whether the sparging process had affected the composite properties. This type of study followed closely along the lines of studies by Menendez et. Al. [5] but involve the use of two different pitches and two sparge gas environments.
3 EXPERIMENTAL PROCEDURES

3.1 Samples

All the gas sparged pitches produced in this study were prepared from two binder pitches designated A and B. The pitches are produced commercially by different manufacturers. Selected properties of the two pitches are given in table 10. These properties were determined by the methods described later in this section and were found to be in good agreement with data from the manufacturers (included in brackets where data is available).

<table>
<thead>
<tr>
<th>Table 10. Characteristic data for pitches A and B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point / °C</td>
</tr>
<tr>
<td>Carbon Yield / %</td>
</tr>
<tr>
<td>Pentane Insolubles / %</td>
</tr>
<tr>
<td>Toluene Insolubles / %</td>
</tr>
<tr>
<td>Quinoline Insolubles / %</td>
</tr>
</tbody>
</table>

Pitch A has been hot filtered to remove the coke particles which explains its low quinoline insoluble content compared to pitch B.

3.2 Pitch Sparging

Each pitch was gas-sparged with oxygen or hydrogen for 1, 2 and 4 hours as described below.

The reaction vessel used for gas sparging is shown in figure 80. The vessel was produced entirely from the nickel alloy, Inconel 601. This alloy material was necessary as previous work using 316 stainless steel showed considerable embrittlement due to either hydrogen dissolution or carbide precipitation at the grain boundaries leading, ultimately, to catastrophic failure.

The reaction vessel was charged with three hundred grams of unground pitch. A flow of nitrogen of 5 l min⁻¹ was introduced into the reaction vessel through a 16μm sintered nickel pad. For sparging with hydrogen or oxygen either a 5%
hydrogen atmosphere (250 ml min\(^{-1}\)) or a 1% oxygen atmosphere (50 ml min\(^{-1}\)) was introduced into the reactor vessel. The gases were supplied via calibrated flow meters to ensure accurate gas composition and flow rate.

Figure 80. Gas-sparge reactor
The reactor vessel was then heated to 400°C at the rate of 3°C min⁻¹ by two metal heaters surrounding the reactor vessel which provided a peak power of 2kW. The use of two heaters was necessary due to the considerable difference in thermal mass between upper and lower regions of the reactor. The gas inlet tube was heated simultaneously so that incoming gases were maintained at the same temperature as the inside of the reactor. The three heated zones were controlled independently by Eurotherm 91e PID controllers. Heating the vessel up to 400°C took approximately 40 minutes.

The gases passed through the pitch which became molten as the temperature increased, and then passed over the baffle system which prevented pitch being carried out of the vessel with the escaping volatiles. The upper region of the vessel containing the baffle system was, in fact, maintained at a slightly higher temperature than the rest of the reactor so that volatilised species did not reflux back into the reactor. Exhaust gases were then passed through a particulate bed with particle size gradation to trap the fine aerosol precipitate of volatile matter.

Once the reactor had reached 400°C it was maintained at this temperature for either 1, 2 or 4 hours and the reactor was then allowed to cool freely to room temperature. When the temperature reached around 100°C the pitch had re-solidified and the gases were switched off. Cooling to around 100°C took approximately 90 minutes.

When the reactor had reached room temperature the re-solidified pitch was recovered from the vessel and the approximate weight determined. A percentage yield of the sparged pitch was then estimated.

A total of fourteen different pitches were obtained including the untreated pitches and pitches that were sparged for 1, 2 or 4 hours in an oxygen or hydrogen atmosphere.
3.3 Pitch Characterisation

3.3.1 Softening point

Pieces of pitch that passed a 2.8 mm mesh were placed into a shallow 6.25 mm hole machined into the surface of a copper block which itself was placed on a hot plate and wrapped in a tape heater. The temperature of the mount was monitored using a thermocouple inserted below the sample-well. The temperature of the mount was raised at a rate of 3°C min⁻¹ using the two heating devices. The pieces of pitch were observed and the softening point was taken to be the temperature at which the angles of the pieces began to smooth out indicating the material had softened. This method was repeated twice for each pitch to obtain an average softening point. The use of this non-standard method was considered preferable to the established ring and ball method since quantities of pitch available from each sparge run were small. Comparison of the measured data with manufacturers’ R&B measurements on the untreated pitches shows good agreement to within 5°C.

3.3.2 Carbon yield

Thermogravimetric analysis was used to determine the carbon yields of the pitches as described here. About 0.25g of powdered pitch was weighed into a ceramic crucible. This was hung from a Cahn D-100 series microbalance and the whole assembly was enclosed inside a silica tube. The part of the silica tube containing the crucible was, itself, situated inside a furnace. A nitrogen atmosphere was maintained inside the tube and the furnace was heated to 1100°C at the rate of 3°C min⁻¹. This temperature was maintained for 1 hour and then the temperature was decreased at the same rate to 20°C. The change in weight of the sample in the crucible was recorded as a function of time and this was converted to a reading of change in weight as a function of temperature. This data was used in conjunction with the value of the final change in weight of the sample to calculate the percentage weight loss as a function of temperature. The final percentage weight loss and hence the percentage carbon yield were calculated.
3.3.3 Pitch solubility

The solubility of pitches in pentane, toluene and quinoline were determined using a modified ASTM method [158]. One gram of <212μm pitch and 50 ml of the solvent under study were placed in a 100ml round bottomed flask. The pentane and toluene solubilities were determined in a slightly different way to the quinoline solubilities. The pentane and toluene pitch mixtures were heated to their boiling points and refluxed for exactly 20 minutes with continuous applied agitation. The pentane mixtures were then immediately filtered using Gooch crucibles with ceramic plate no. 4. The toluene mixtures were all cooled to exactly 50°C and then filtered. It was important to filter each toluene mixture at the same temperature as a preliminary experiment on pitch BH1 proved that the toluene insoluble percentage was dependent on filter temperature. The results of this preliminary experiment are given in table 11 below. It is clear that as the filter temperature was increased, the toluene soluble percentage increased.

Table 11. Effect of filter temperature on toluene insolubles

<table>
<thead>
<tr>
<th>Filter Temperature / °C</th>
<th>Toluene % solubles for pitch BH1</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td>40</td>
<td>57</td>
</tr>
<tr>
<td>50</td>
<td>58</td>
</tr>
</tbody>
</table>

The crucibles containing the pentane or toluene insoluble fraction were rinsed with three 10ml aliquots of solvent. The crucibles were dried in an oven set at 10°C above the solvent boiling point overnight. The crucibles were weighed to find the weight of the insoluble pitch remaining in the crucible and hence the percentage insoluble fraction of the pitch was calculated.

The quinoline mixtures could not be refluxed as the boiling point of quinoline is above the softening points of the pitches. The quinoline and pitch mixtures were heated to 85°C over a boiling water bath and maintained at this temperature for 20 minutes with continuous applied agitation. The quinoline and pitch mixtures were filtered immediately after the 20 minutes with ceramic plate no. 2. No. 4 pads could not be used for quinoline as they quickly became blocked by the viscous quinoline.
containing a large amount of dissolved pitch. The crucibles containing quinoline insolubles were dried in an oven at 100°C overnight and the final weight of the quinoline insolubles was measured. The percentage weight of the quinoline insoluble fraction was thus determined.

3.3.4 Determination of errors in softening point, carbon yield and solubilities

The standard error in each measured parameter was determined by six-fold repeat measurement on a single sample of pitch. Batch to batch errors were also assessed by four-fold duplication of the data for sample BH2. The reason for choosing a 2-hour sparged sample was that experience had shown that the two hour data exhibited the highest variability of the three time periods studied. The choice of pitch type and process gas was arbitrary.

3.3.5 Optical microscopy of the pitches

Pieces of pitch were embedded in epoxy resin and polished using silicon carbide papers and then with 1µm alumina powder and finally with 0.05 µm γ alumina powder on a cloth pad. In some cases the surface was smeared with resin before the final polishing stages to ensure good filling of the pores with resin. The mounted, polished samples were examined under a xenon light source microscope fitted with crossed polars and a full wave retarder plate (λ-plate). Any anisotropic areas show up as yellow or blue isochromatic areas and isotropic areas are purple. Micrographs at magnification 50× were taken of all the pitches. The micrographs were observed to determine whether there was evidence of any mesophase formation.
3.4 Composite Fabrication

The raw materials required for fabrication of the composites are carbon fibre cloth and carbon matrix precursors. The matrix precursors that were used in this work were the 14 pitches that have been obtained from the first part of the project. The properties of these pitches are given in table 14. The next section looks at the properties of the carbon fibre cloth that was used and the following sections review the methods used for the initial press-moulding stage and the re-impregnation stages of composite fabrication.

3.4.1 Characteristics of the carbon fibre cloth

The carbon fibres in the carbon fibre cloth that was used are PAN-based Toray M40 fibres. This specific carbon fibre cloth was chosen primarily because the fibres were not sized. The properties of these fibres are summarised in table 12 below.

Table 12. Properties of Toray M40 filaments

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength / MPa</td>
<td>2740</td>
</tr>
<tr>
<td>Tensile modulus / GPa</td>
<td>392</td>
</tr>
<tr>
<td>Elongation to failure / %</td>
<td>0.7</td>
</tr>
<tr>
<td>Density / g cm$^{-3}$</td>
<td>1.81</td>
</tr>
<tr>
<td>Filaments per tow</td>
<td>3000</td>
</tr>
</tbody>
</table>

The properties of the carbon fibre cloth are summarised in table 13 below.
Table 13. Properties of the carbon fibre cloth

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ends per cm</td>
<td>4.92</td>
</tr>
<tr>
<td>Picks per cm</td>
<td>4.92</td>
</tr>
<tr>
<td>Weave</td>
<td>Plain</td>
</tr>
<tr>
<td>Nom. Wt.</td>
<td>197 g m</td>
</tr>
<tr>
<td>Nom. Thickness</td>
<td>0.30 mm</td>
</tr>
<tr>
<td>Warp count</td>
<td>200 tex</td>
</tr>
<tr>
<td>Weft count</td>
<td>200 tex</td>
</tr>
</tbody>
</table>

3.4.2 Press-moulding the composites

The first stage in the fabrication of the carbon-carbon composites in this work was the press-moulding. During this process the carbon-fibre cloth is layered up with alternate layers of powdered pitch in a mould. The mould is then heated and pressed to allow the pitch to infiltrate the pores in the cloth.

The mould used to make the composites is shown schematically in figure 81 below.

Figure 81. Diagram of the closed mould
The three parts of the mould are detachable. The bottom piece of the mould is a flat rectangular piece of steel. The middle piece is a rectangular block with a rectangular hole in its centre. When the middle piece is put on top of the bottom piece so that the hole in the middle piece is closed off on one side, a cavity with a solid bottom exists. This is the cavity in which the carbon fibre cloth and pitch can be layered up. The dimensions of the cavity were 10.2 cm long by 2.4 cm wide and approximately 2.5 cm in depth. The top piece of the mould has a rectangular protrusion that fits into the rectangular cavity created by the bottom and middle pieces. The protrusion is slightly smaller in length and width than the hole so that clearances are left on four sides of the protrusion when it is inside the cavity. The clearances are for excess pitch to run out during pressing.

Steel spacers of width 4.5 mm were placed in between the top and middle pieces of the mould on either side of the cavity. These prevent the base of the protrusion of the top piece from getting any nearer to the base of the cavity than 4.5 mm and thus the composite is restricted to a minimum thickness of 4.5 mm.

The carbon fibre cloth was cut, using sharp scissors, into pieces of approximately 10.2 cm by 2.4 cm, to fit very closely into the mould cavity. Twelve of these pieces of cloth were layered up into the mould cavity with 13 layers of 1.4 g of \(<212\ \mu\text{m}\) powdered pitch. Preliminary experiments showed that this number of layers fitted the mould without bursting out during pressing. This large amount of pitch between each layer of cloth was required because during pressing a lot of pitch leaked out of the mould via the clearances.

After preliminary experiments it was also found that the pitch was becoming very liquid and running out of the mould. There was not enough pitch remaining in the mould to bind the layers of cloth together. It was decided to coat the carbon fibre cloth with 1M potassium nitrate solution (KNO₃) to form oxygen linkages within the pitch which would make it more viscous and less likely to run out. The coated pieces of cloth were allowed to dry before layering up.

Once all the cloth and pitch was layered up, the mould was heated to 250°C at the rate of 3°C / min by three cartridge heaters, one fitting into each layer of the mould, as shown in figure 81. The heaters were all controlled by one Eurotherm 91e
PID controllers with positive feedback from three thermocouples, again, one in the centre of each layer of the mould.

When the mould reached 250°C it was pressed under a load of 6 tons for 0.5 hour. This was to force the molten pitch into the fibres of the cloth and to press the composite to a constant thickness of 4.5mm. After pressing the 4.5 mm spacers were replaced by 3 mm spacers so that the composite could be re-pressed to a thickness of 3 mm. This depth was chosen as many manufacturers of carbon-carbon composites make composites of 3mm thickness.

The mould was then heated again at the rate of 3°C/min to 400°C at which point the mould was pressed for the second time under a load of 6 tons for 0.5 hour, to the constant thickness of 3 mm. At 400°C the molten pitch was more fluid and flowed more readily into the cloth under the applied pressure.

After pressing the composite was allowed to cool overnight and then removed from the mould. The edges of the cuboid composite were trimmed to remove stray fibres and pitch.

The composite was then placed in a furnace in a nitrogen atmosphere to be carbonised. The furnace was heated up to 1000°C at the rate of 3°C per min. It was maintained at 1000 °C for 1 hour then brought back down to room temp at 3°C per min. During carbonisation, the composite was restrained between two carbon plates transverse to the layers to prevent bloating by the release of volatiles from the pitch during carbonisation. The plates also prevented some of the molten pitch from running out of the composite at the early stages of carbonisation. At this stage the composite was complete and ready for re-impregnation with pitch.

3.5 Composite Re-impregnation

The next stage of the fabrication of the carbon-carbon composites is the re-impregnation with pitch. The apparatus used for re-impregnation of the composites is shown schematically in figure 82 below.
The composite to be reimpregnated was placed in the boiling tube which was then filled with powdered pitch. The powdered pitch used to re-impregnate a composite must be the same type as the pitch that was initially used in the press-mould stage of fabrication of that composite. The boiling tube was attached to a rotary pump and a vacuum slowly applied so as not to cause the powdered pitch to be forced into the pump. The vacuum pump removed air and water vapour from the system.

While still evacuating, the boiling tube was heated in a furnace controlled by a Eurotherm 91e PID controller at the rate of 5°C / min to 250°C. During heating more water evaporated and was evacuated from the system. When the furnace reached 250°C it was maintained at this temperature for around 20 minutes until the pitch in the boiling tube had also attained 250°C. At this point the vacuum was removed and atmospheric pressure was re-established within the boiling tube. The increase in pressure forced the molten pitch into the pores in the composite. The pitch and composite were kept at 250°C at atmospheric pressure for 10 minutes before both were removed from the tube.

The composite was then left to cool to room temperature. Excess pitch was scraped from the outside of the composite, care being taken not to damage the
composite. Finally, the re-impregnated composite was carbonised as before. The composite was again, under restraint by two carbon plates. The furnace was heated to 1000°C at 3°C per min, maintained at 1000°C for 1 hour and then brought back to room temperature at 3°C per min.

This re-impregnation stage was repeated twice more but for the second and third impregnations the composites were heated to 350°C instead of 250°C. The reason for this was that the pitches were still very viscous at 250°C and the increase in density after the first impregnation was small. A temperature of 350°C was chosen because the pitches had been sparged at 400°C and so did not lose any additional volatiles during re-heating to 350°C. The higher temperature caused a decrease in viscosity such that more pitch filtered into the pores of the composites. The density increase after the second impregnation was larger than after the first and so the increase in temperature was successful. The increase in density after the third impregnation was less than after the second and it was predicted that further impregnations would only give small density increases. Hence no further impregnations were carried out after the third.
3.6 Composite Bulk Density Determination

The bulk densities, $\rho_B$, of the composites were determined by simple application of the formula:

$$\rho_B = \frac{m}{V_B} \quad (1)$$

where $m$ is the mass of the solid composite and $V_B$ is the bulk volume of the solid composite. The masses of the dried samples were found using a 4 decimal place balance. The volumes of the samples were determined by measuring the length, width and depth of the samples. Each dimension was measured in three different places on the composite such that three densities for each composite were calculated and a mean density was determined. The samples were uniform cuboids and three measurements lead to a standard error in the bulk densities of $\pm 0.06 \text{ g/cm}^3$.

This method of bulk density determination was found to be more accurate than the mercury immersion method. The mercury immersion method resulted in values for bulk density that were inaccurate due to the entrapment of air on the rough composite surface.

3.7 True Density, Open, Closed and Total Porosity Determination by Helium Pycnometry

The true density of a material is defined as being the ratio of the mass to the volume occupied by that mass. This volume does not include pores or cracks that may be present in a solid sample of the material and so finely powdered samples are used for true density determination. However, the fine powders may, themselves, still contain some porosity leading to error in the density.

Even if a solid sample contains no porosity its true density works out to be different to that of a fine powder of the same material. This is due to the fact that during the preparation of many powders, atoms and molecules near the surface are often forced out of their equilibrium positions within the solid structure and so the measurement of density is affected. Hence using a powdered sample to find the
density of a solid structure does not give a completely correct value of the density of the solid structure but values are useful to make comparisons.

Helium pycnometry was the method used to determine true densities of the composites. A schematic diagram of the Micromeritics Multivolume Helium Pycnometer 1305, used for our sample, is shown in figure 83.

Figure 83. Schematic diagram of the Micromeritics Multivolume Helium Pycnometer 1305.
The volumes of the sample cell and the reference volume are $V_c$ and $V_R$ respectively. There were three choices of sample cell volume: 5, 35 and 105 cm$^3$. Three corresponding reference volumes may be utilised by combinations of valves $V_2$ and $V_3$ being open or closed. The smallest reference volume that the sample will fit into is selected as this minimises the volume percentage error. The sample cell volume that was chosen for the solid samples was the 35 cm$^3$ cell and the volume chosen for the powdered sample was the 5 cm$^3$ cell.

The sample was placed in the sample cell and the system was purged with helium by alternately having the fill valve open and vent valve closed and then the fill valve closed and vent valve open (with valve $V_1$ open throughout). After purging the vent valve was left open until the system acquired the ambient pressure at which time it was closed. Valve $V_1$ was then closed. The pressure in the sample cell was then increased, by opening the fill toggle, to a pressure, $P_1$, approximately 1 atm above the ambient. The fill toggle was closed and pressure $P_1$ was allowed to equilibrate for 30 seconds. $P_1$ was then recorded. Valve $V_1$ was opened, and the gas was expanded into the reference volume, $V_R$. The new pressure of the system, $P_2$, was recorded.

The volume of the sample in the cell, $V_s$, is calculated by simple application of equation (2), below, which is derived from the gas laws.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (2)$$

Assuming temperatures $T_1$ and $T_2$ are equal, then application of this equation to the above system yields the equation for $V_s$ below:

$$V_s = V_c + \frac{V_R}{1 - \frac{P_1}{P_2}} \quad (3)$$

$V_c$ and $V_R$ were first determined by performing a run with no sample in the sample cell and by performing a run with a sample of known volume, $V_{\text{CALIB}}$, in the sample cell (a steel ballbearing, just smaller than the sample cell itself).
Once $V_s$ has been found the true density, $\rho_{\text{true}}$, may readily be calculated using

$$\rho_{\text{true}} = \frac{m_s}{V_s}$$

(4)

where $m_s$ is the mass of the sample.

The porosity was calculated from the helium pycnometry true density, $\rho_{\text{true}}$, and the composite bulk density, $\rho_B$, according to the formula:

$$V_p = \left(1 - \frac{\rho_B}{\rho_{\text{true}}}\right)100$$

(5)

where $V_p$ is the volume fraction of pores. $V_p$ is equal to the open porosity, $\text{OP}$, when solid pieces of composite are used and is equal to the total porosity, $\text{TP}$, when powdered composite was used. The closed porosity, $\text{CP}$, is readily calculated by

$$\text{CP} = \text{TP} - \text{OP}$$

(6)

Solid samples of about 4.5g and powdered samples of about 3g were used in 15cm$^3$ and 5cm$^3$ sample cells, respectively. The standard error in the true densities and porosities were found by six-fold repeat of their determination using one sample. The standard error in true density was 0.004 g/cm$^3$ and the standard errors in OP and TP were both 0.2%. The standard error in CP worked out to be 0.3%.

### 3.8 Optical Microscopy of the Composites

The composites were cut, using a diamond saw, into small rectangular pieces with edges parallel to the composite edges which are indeed parallel to the two fibre directions. The inner structures of the composites were thus exposed. Longitudinal sections of composite were embedded in epoxy resin and polished using silicon carbide papers and then with 1µm alumina powder and finally with 0.05 µm γ alumina powder on a cloth pad. In some cases the surface was smeared with resin before the final polishing stages to ensure good filling of the pores with resin. The
mounted, polished samples were examined under a xenon light source microscope fitted with crossed polars and a full wave retarder plate (\(\lambda\)-plate). Any anisotropic areas show up as yellow or blue isochromatic areas and isotropic areas are purple. Micrographs at magnification 50\(\times\) were taken of all the composites. Micrographs of each composite were taken to show fibres parallel to the cutting direction and fibres perpendicular to the cutting direction. Micrographs of the sample edges were taken and as well as micrographs of selected, representative pores.

### 3.9 Flexural Strength and Modulus Determination

Initially it was intended to measure the inter-laminar shear strength of the composites but the test specimens failed by brittle fracture and consequently it was decided that the data was more appropriate to determination of flexural properties.

The flexural properties of the composites were measured using a three point bend test during which tension, compression and shear loading are imposed on the sample simultaneously. The apparatus used to perform the test was a standard Instron machine. It is usual, when determining flexural properties of a material, to use a high span to thickness ratio of about 32:1 so that the samples are more likely to fail in bending rather than in shear. The sample pieces only had a span to depth ratio of around 5:1, being 15mm in span and 3mm in depth because they were initially prepared for interlaminar shear strength determination which requires this low span to depth ratio. The low span to depth ratio meant that the flexural properties were not comparable to data measured using specimens with high span to depth ratios but were useful to draw comparisons between the specimens prepared in this work. The flexural strength, \(\sigma_f\), and modulus, \(E_f\), are calculated as follows:

\[
\sigma_f = 14.715 \frac{PL}{wd^2}, \text{ (MPa)} \tag{1}
\]

\[
E_f = \frac{L^3m}{4wd^3}, \text{ (GPa)} \tag{2}
\]
where

\[ P = \text{load at failure, kg} \]
\[ L = \text{span, mm} \]
\[ w = \text{width, mm} \]
\[ d = \text{specimen depth, mm} \]
\[ m = \text{slope of the load-deflection curve in the elastic deformation range, N/m} \]

The results quoted are mean values calculated from 9 specimens for each type of composite. The standard errors were of the order of 69 MPa for flexural strength and 29 GPa for flexural modulus.
4 RESULTS AND DISCUSSION

In this section the results for the characterisation of the pitches are presented and discussed and then the properties of the composites made from the pitches are presented and discussed. The characterisation of pitches is compared to the characterisation of composites to determine any correlation that exists.

4.1 Pitch Characterisation

Table 14 below gives the measured properties of the two pitches A and B when untreated and when sparged with hydrogen and oxygen for 1, 2 and 4 hours. The standard errors are given (at the top of the table) along with the batch to batch errors (at the foot of the table).

Table 14. Properties of gas sparged pitches

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Treatment</th>
<th>SP (°C) ± 6°C</th>
<th>CY (%) ± 0.7%</th>
<th>ΔCY/ΔSP</th>
<th>PI (%) ± 1%</th>
<th>TI (%) ± 4%</th>
<th>QI (%) ±0.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>84</td>
<td>36.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1H</td>
<td>H₂/1 hour</td>
<td>218</td>
<td>56.5</td>
<td>0.15</td>
<td>97</td>
<td>43</td>
<td>0.5</td>
</tr>
<tr>
<td>A1H2</td>
<td>H₂/2 hours</td>
<td>210</td>
<td>51.1</td>
<td>0.12</td>
<td>98</td>
<td>41</td>
<td>0.9</td>
</tr>
<tr>
<td>A1H4</td>
<td>H₂/4 hours</td>
<td>255</td>
<td>62.4</td>
<td>0.15</td>
<td>97</td>
<td>54</td>
<td>1.0</td>
</tr>
<tr>
<td>A01</td>
<td>O₂/1 hour</td>
<td>192</td>
<td>50.4</td>
<td>0.13</td>
<td>93</td>
<td>36</td>
<td>1.0</td>
</tr>
<tr>
<td>A02</td>
<td>O₂/2 hours</td>
<td>185</td>
<td>48.3</td>
<td>0.12</td>
<td>94</td>
<td>38</td>
<td>1.3</td>
</tr>
<tr>
<td>A04</td>
<td>O₂/4 hours</td>
<td>237</td>
<td>61.2</td>
<td>0.16</td>
<td>96</td>
<td>57</td>
<td>1.3</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>111</td>
<td>37.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1H</td>
<td>H₂/1 hour</td>
<td>178</td>
<td>48.8</td>
<td>0.16</td>
<td>96</td>
<td>42</td>
<td>3.2</td>
</tr>
<tr>
<td>B1H2</td>
<td>H₂/2 hours</td>
<td>206</td>
<td>54.4</td>
<td>0.17</td>
<td>96</td>
<td>51</td>
<td>5.0</td>
</tr>
<tr>
<td>B1H4</td>
<td>H₂/4 hours</td>
<td>245</td>
<td>60.4</td>
<td>0.17</td>
<td>100</td>
<td>58</td>
<td>4.8</td>
</tr>
<tr>
<td>B01</td>
<td>O₂/1 hour</td>
<td>189</td>
<td>55.1</td>
<td>0.22</td>
<td>94</td>
<td>46</td>
<td>2.6</td>
</tr>
<tr>
<td>B02</td>
<td>O₂/2 hours</td>
<td>188</td>
<td>56.5</td>
<td>0.24</td>
<td>96</td>
<td>47</td>
<td>3.1</td>
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<tr>
<td>B04</td>
<td>O₂/4 hours</td>
<td>233</td>
<td>63.9</td>
<td>0.21</td>
<td>98</td>
<td>60</td>
<td>4.9</td>
</tr>
<tr>
<td>Batch errors</td>
<td>±23</td>
<td>±14</td>
<td>±1</td>
<td>±7</td>
<td>n/d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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In general the error margins of the measured parameters are small. Batch to batch errors, on the other hand, are large. The reason for large batch to batch errors is considered to be due to the control of the process reactor. The reactor can only be heated up with the sparge gas flowing since gas flow is required to stop molten pitch running through the sintered plate. This means that each batch receives a variable process time while the vessel heats up for approximately 40 minutes and while it cools down to below the softening point of the pitch when the gas flow may be turned off. The cooling down takes up to 90 minutes. This overall variable time is large compared to process times, hence batch variability is likely to be great. This batch variability may account for the occasional anomalous entry in the table. However, batch to batch variability is unimportant to this work, as the requirement was for a range of pitches with relatively different degrees of thermal treatment and this was achieved.
4.2 Sparge Reactor Yields

Yields from the gas sparge reactor are approximate as it is impossible to account for all the mechanical losses in unloading the reactor. The data for pitch yield from the sparge reactor is shown in table 15 below.

Table 15. Sparge percentage yields

<table>
<thead>
<tr>
<th>Sparge Time/ Hours</th>
<th>Sparge % Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AH</td>
</tr>
<tr>
<td>1</td>
<td>56.7</td>
</tr>
<tr>
<td>2</td>
<td>65.7</td>
</tr>
<tr>
<td>4</td>
<td>50.2</td>
</tr>
</tbody>
</table>

Figure 84 is a plot of the sparge percentage yield as a function of sparge time for the four combinations of pitch and pitch treatment.

Figure 84. Graph of sparge percentage yield vs. sparge time
The yields range from 50 to 75% by weight. It is generally true that longer sparge times result in lower yields. This is expected as more volatiles will be lost, the longer the sparge time, assuming that volatile evolution is continuous throughout the sparging process.

It can be seen that yields from pitch B are higher than for pitch A. This may be due to the fact that pitch B has a higher softening point than pitch A and thus it probably contains molecules with a higher average molecular weight that are less likely to volatilise.

For both pitches the oxygen treatment results, in general, in higher yields than the hydrogen treatment. This suggests that the hydrogen and oxygen treatments involve different chemical processes rather than the sparging being a simple volatile stripping process.
4.3 Pitch Softening Points

The data for pitch softening points is included in table 14. The softening points, SP's, range from 84°C for pitch A to 255°C for pitch AH4. Figure 85 shows the variation of softening point with sparge time for the two pitches treated with hydrogen and oxygen.

Figure 85. Graph of pitch softening point vs. sparge time

For all cases there was a marked increase in SP in the early stages of sparging, up to 1 hour. This rate of increase in SP reduced over the following three hours.

Between 1 and 2 hours there was evidence for a decreased SP for two cases, AH and BO and between 2 and 4 hours the SP's of these two pitches increase again. The SP's other two pitches, AO and BH, increase between 1 and 2 hours and level off between 2 and 4 hours.

Comparing hydrogen sparging to oxygen sparging, both pitches A and B have higher SP's after sparging with hydrogen which contrary to expectation. We might have expected the oxygen sparged pitches to have the higher SP’s due to formation of ether linkages or oxidative growth mechanisms. However, the difference in SP's due
to different sparge gases does indicate that different chemical processes may be occurring for the hydrogen and oxygen treatments.

Comparing the two pitches with each other after treatment with hydrogen, pitch A has a higher SP than pitch B. After treatment with oxygen the SP's of the two pitches are very similar.

4.4 Optical Microscopy of the Pitches

The micrographs of all the pitches show that neither pitch, at any stage of sparging, contains any mesophase whatsoever. Micrographs of the Pitches A, AH4 and AO4 shown in figure 86. Micrographs of the Pitches B, BH4 and BO4 are shown in figure 87. All of these micrographs have visible surface scratches that could not be polished away due to the very soft nature of the pitches. Some residual alumina powder is also present and shows up as yellow-green areas that should not be confused with anisotropy.

The only regions of anisotropy present are those in pitch B and in derivatives of pitch B which are, in fact, pieces of coke. These pieces of coke may, at least partially, explain the higher QI and TI fractions in pitch B compared to pitch A which does not contain any coke particles. Figure 88 is included for comparative purposes and shows the development of mesophase in coal tar pitch at early and later stages.
Figure 86. Optical Micrographs of pitches (×35) (a) A, (b) AH4 and (c) AO4
Figure 87. Optical Micrographs of pitches (×35) (a)B, (b)BH4 and (c)BO4
Figure 88. Optical micrographs of mesophase development in coal tar pitch

(×470) (a) early stages, (b) later stages
4.5 Pitch Weight Losses During Thermal Gravimetric Analysis

Figures 89-92 are the graphs of percentage weight loss versus temperature obtained during the carbonisation of each type of pitch in a nitrogen atmosphere up to 1100°C. Each graph shows a steady increase in weight loss to a maximum loss after which any increase in temperature does not result in any further weight loss. The TGA of selected samples has been repeated and these duplicate results are also presented in figures 89-92. It is clear that the repeatability of these results is extremely good as illustrated, for example, by the two curves for pitch AH1 in figure 89, which are virtually on top of another. The maximum weight losses were used to calculate the carbon yields of the pitches which are presented in the next section.
Figure 89. Graph of percentage weight loss during carbonisation of pitch A treated with hydrogen for various times vs. temperature

Figure 90. Graph of percentage weight loss during carbonisation of pitch A treated with oxygen for various times vs. temperature
Figure 91. Graph of percentage weight loss during carbonisation of pitch B treated with hydrogen for various times vs. temperature

Figure 92. Graph of percentage weight loss during carbonisation of pitch B treated with oxygen for various times vs. temperature
The temperatures at which the maximum weight loss occurs for all the pitches are given in Table 16 below. The temperatures of maximum weight loss range from 522-582°C. This is a small range of temperatures. This indicates that all the pitches are similar in composition and have all lost all their volatile content by 582°C. There is no obvious trend in the temperatures of maximum weight loss.

Table 16. Temperatures of maximum weight loss during thermal gravimetric analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at which Maximum Weight Loss Occurs / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>556</td>
</tr>
<tr>
<td>AH1</td>
<td>582</td>
</tr>
<tr>
<td>AH2</td>
<td>541</td>
</tr>
<tr>
<td>AH4</td>
<td>565</td>
</tr>
<tr>
<td>AO1</td>
<td>560</td>
</tr>
<tr>
<td>AO2</td>
<td>522</td>
</tr>
<tr>
<td>AO4</td>
<td>528</td>
</tr>
<tr>
<td>B</td>
<td>558</td>
</tr>
<tr>
<td>BH1</td>
<td>539</td>
</tr>
<tr>
<td>BH2</td>
<td>558</td>
</tr>
<tr>
<td>BH4</td>
<td>564</td>
</tr>
<tr>
<td>BO1</td>
<td>556</td>
</tr>
<tr>
<td>BO2</td>
<td>545</td>
</tr>
<tr>
<td>BO4</td>
<td>564</td>
</tr>
</tbody>
</table>
4.6 Carbon Yields

The carbon yields were calculated using the maximum weight loss data. The data for the carbon yields of the pitches is given in table 14. Figure 93 shows the variation of carbon yield, CY, with sparge time for the two pitches treated with hydrogen and oxygen.

![Graph of carbon yield vs. sparge time](image)

**Figure 93. Graph of carbon yield vs. sparge time**

The trends in CY are similar to the trends in SP's. For all cases there was a marked increase in CY in the early stages of sparging, up to 1 hour. This rate of increase in CY reduced over the following three hours.

Between 1 and 2 hours there was evidence for a decreased CY for two cases: AH and AO, and between 2 and 4 hours the CY's of these two pitches increase again. The CY's of the other two pitches, BH and BO, increase between 1 and 2 hours and increase again between 2 and 4 hours, but to a lesser degree than AH and AO.
Comparing oxygen to hydrogen sparging: For pitch A, hydrogen treatment gives the higher CY's and for pitch B the oxygen treatment gives higher CY's i.e. the treatment that gives the higher CY depends on the starter pitch. This suggests that the different sparge gases have different effects on the two pitches.

Comparing the two types of pitch: For treatment with hydrogen, pitch A after 4 hours of sparging has the higher CY and for treatment with oxygen pitch B has higher CY's i.e. the pitch that gives the higher CY depends on the treatment. This suggests that the two pitches behave differently to each other during sparging with either gas.
4.7 Pitch Solubilities

The data for the solubilities of the pitches are given in table 14.

4.7.1 Solubility in pentane

Figure 94 shows the variation of pentane insolubles, PI, with sparge time for the two pitches treated with hydrogen and oxygen. All pitches were very insoluble in pentane and the PI fraction ranges from 84% in pitch A to 100% for pitch BH4.

The largest changes in solubility were seen after 1 hour of sparging where the percentage of insolubles for all pitches increased. Between 1 and 2 hours there were small changes for all pitches. Between 2 and 4 hours the percentage insolubles increased again for all the pitches except pitch A treated with hydrogen whose PI value remained constant since the value after 1 hour of sparging. This suggests that a maximum value of pentane insolubles has been reached i.e. no more material can be converted to pentane insoluble material and no material can be converted to pentane soluble material.

Comparing the hydrogen sparging to oxygen sparging, the hydrogen sparged pitches had higher PI's than the oxygen sparged ones. Comparing pitches A and B, the hydrogen treatment gave similar PI's for both pitches and for oxygen sparging the PI's were higher in pitch B.

4.7.2 Solubility in toluene

Figure 95 shows the variation of toluene insolubles, TI, with sparge time for the two pitches treated with hydrogen and oxygen. The pitches were much more soluble in toluene than in pentane. The insoluble fraction ranges from 22% in pitch A to 60% in pitch BO4. This is a large range of insolubilities compared to the ranges for pentane insolubles and quinoline insolubles.

There was a significant increase in toluene solubles for all pitches after 1 hour of sparging. Between 1 and 2 hours there were small changes in solubility except for pitch B treated with hydrogen which had a larger increase in TI in this time interval.
Between 2 and 4 hours all the pitches increased their insoluble fraction but pitch B treated with hydrogen showed a smaller increase than the others subsequent to its larger increase between 1 and 2 hours.

Comparing the hydrogen sparging to oxygen sparging, for both the pitches the hydrogen and oxygen treatments gave similar values of TI. Comparing pitches B and A, pitch B always has higher TI fraction than the pitch A. This is likely to be at least partly due to the fact that pitch B contains coke particles which are probably partly toluene insoluble whereas pitch A has been hot filtered to remove coke particles.

4.7.3 Solubility in quinoline

Figure 96 shows the variation of quinoline insolubles, QI, with sparge time for the two pitches treated with hydrogen and oxygen. The pitches were much more soluble in quinoline than they were in pentane or toluene. The QI fraction ranges from 0.1% in pitch A to only 4.9% in the pitch BO4.

All pitches showed an increase in QI’s after 1 hour. Between 1 and 2 hours the QI fraction shows an increase of the same order as the 0-1 hour increase which was different to the trend between 1 and 2 hours for all the other properties. The trend between 2 and 4 hours was also different to the other properties in that the QI fraction remains the same for all pitches (except pitch B treated with oxygen where there is another increase in insolubles after 4 hours).

Comparing the hydrogen sparging to oxygen sparging, for pitch A the oxygen treatment gives higher QI’s than the hydrogen treatment. For pitch B the hydrogen treatment yields higher QI’s than the oxygen treatment. Comparing pitch A to pitch B, pitch B always has a higher QI fraction than pitch A. This is again likely to be at least partly due to the fact that pitch B contains coke particles which are quinoline insoluble and pitch A does not.
Figure 94. Graph of pentane insolubles vs. sparge time

Figure 95. Graph of toluene insolubles vs. sparge time

Figure 96. Graph of quinoline insolubles vs. sparge time
4.8 Model for Pitch Sparging

To analyse the data for the properties of the pitches it is useful to postulate a mechanism by which pitch is hardened in the gas sparging process. The data may then be fitted to this model to see whether or not chemical reactions are involved.

The simplest model for the hardening of pitch is one in which the pitch is comprised of two fractions. One fraction includes molecules which produce carbon on pyrolysis and the other which comprises molecules which are volatile and evaporate during pyrolysis. This model does not account for molecules changing from one type to the other during pyrolysis.

Let $W_c$ be the weight fraction of carbon producing molecules and $W_v$, the weight fraction of volatile molecules. Let the carbon yield, expressed as a weight fraction, obtained from pyrolysis of the raw pitch be $C$ and that of the gas sparged pitch be $C'$.

If $\nu_c$ is the weight fraction of carbon obtained from the carbon producing phase it follows that the carbon yield, $C$, will be the product of the weight fraction of carbon producing molecules and the weight fraction of carbon produced from these carbon producing molecules:

$$C = \nu_c \cdot W_c \quad (1)$$

This may be rewritten as:

$$C = \frac{\nu_c W_c}{W_c + W_v} \quad (2)$$

Since $W_c + W_v$ is equal to unity.

Similarly, for the gas sparged pitch

$$C' = \frac{\nu_c \cdot W_c}{W_c + W_v - W_l} = \frac{\nu_c \cdot W_c}{1 - W_l} \quad (3)$$

where $W_l$ is the weight fraction of molecules lost during sparging i.e. $1 - W_l$ is the weight fraction of molecules remaining after sparging or the sparge yield.
Substituting (1) into (3) gives

\[ \frac{1}{1-W_1} = \frac{C'}{C} \quad (4) \]

Thus a plot of reciprocal sparge yield vs. the carbon yield of the gas sparged pitch will be a straight line of gradient \(1/C\), the inverse carbon yield of the raw pitch. This predicted value of carbon yield of the raw data may then be compared to the actual experimental value. Any discrepancies will be explained by deviations from the model that has been described.

Figure 97 is the plot of reciprocal sparge yield vs. the carbon yield of the gas sparged pitch for pitch A. The sets of data for both hydrogen and oxygen sparged pitches fall on the same line which has a correlation coefficient \(R^2\) of 0.97. The carbon yield of the raw pitch estimated from the gradient is 28.3% and the experimental value from TGA was 36.3%. These values are within tolerable agreement of each other. The fact that the experimental value is higher than the value from the graph can be explained by the fact that the experimental value is obtained from TGA under quiescent conditions and would itself be lower if pyrolysis has been conducted under conditions of a gas sparged system. The fact that these results are in agreement shows that the carbon producing phase has produced the amount of carbon predicted and hence has not been altered by the sparge process.

Figure 98 is the plot of reciprocal sparge yield vs. the carbon yield of the gas sparged pitch for pitch B. This figure is markedly different than figure 97. The data for oxygen and hydrogen pitches lie on different lines. The hydrogen sparged pitch data gave an estimated carbon yield for the raw pitch of 31% (correlation 0.977). This is lower than the experimental value of 37.9% and may be explained in the same way as for pitch A. So the passage of hydrogen has not altered the carbon producing phase.

The oxygen data lies on a line with a shallower gradient and thus gives a higher value for estimated raw pitch carbon yield of 45% (correlation 0.995). This is not in agreement with the experimental value and is in fact higher than the experimental value. This means that the carbon yield of the sparged pitch, \(C'\), is
higher than the model predicts. The model has not worked in this case and it is concluded that the oxygen sparging has chemically altered pitch B to increase the carbon producing phase at the expense of the volatile matter hence explaining the increased carbon yield of the oxygen-sparged pitch.

It is possible to substitute solvent insolubles data in the place of carbon yield in all the above equations to generate more specific information regarding the chemical changes in the pitches. Unfortunately the data for PI and QI in table 14 exhibit small ranges of values compared to the error in the values. The TI data is much more amenable to analysis. The model assumes that there is a fraction of toluene insoluble molecules that do not volatilise during pyrolysis. Recasting equation (4) in terms of TI data gives

\[
\frac{1}{1-W_i} = \frac{TI'}{TI} \tag{5}
\]

where TI' is the toluene insoluble fraction of the gas sparged pitch that was produced from the raw pitch with toluene insoluble fraction, TI at a yield of 1-Wi.

Plotting the data for pitch A gives figure 99. Both oxygen and hydrogen data fall on the same line. The slope of this line gives an estimated TI value of the raw pitch of 39% (correlation 0.894). This is higher than the experimental value of 22%. Thus the sparged sample contains a higher value of toluene insoluble material than the model predicts (TI' is higher than expected). It may have been expected that the slope would be steep and that TI' was lower than predicted as some of the toluene insoluble molecules were volatilised, but the opposite has occurred. The observed, higher toluene insoluble fraction of the sparged pitch, TI', must be due to combinatory chemistry involving volatile, toluene soluble species combining to give toluene insoluble, non volatile species. However these new molecules do not increase, or affect in any way, the carbon yield.

Figure 100 gives the plot for pitch B. The hydrogen and oxygen data fall on different lines. The hydrogen data gives an estimated TI for the raw pitch of 41.5% (correlation 0.987) which is again above the observed value of 28%. This is explained by the same arguments as for A. The oxygen data gives a reduced slope giving a
predicted TI value of 54% (correlation 0.994), which is much higher than the experimental value.

The increase in predicted TI for the oxygen data (54%) from the value for the hydrogen data (41.5%) is 12.5% and this correlates closely with the increase in predicted carbon yield from the hydrogen data (31%) to the oxygen data (45%) of 14%. This allows us to conclude that the additional toluene insoluble material introduced by oxygen sparging pitch is also carbon-producing.

The data does not indicate the exact nature of the changes in pitch B brought about by oxygen but it is likely that the reaction is either an oxidative molecular growth mechanism or a change in volatility of polyaromatics brought about by the introduction of oxygen functionality. Comparison of napthalene, BP 218°C with 2-napthanol, BP 295°C, can be used to illustrate this point.

In summary, then, the two pitches have shown markedly different results. Pitch A shows evidence of chemical change as measured by an increase in TI with sparging. However this change is independent if the type of sparge gas used and is presumably thermally induced. The chemical change does not increase the carbon yield of the pitch from the increase in carbon yield that occurs due to pyrolysis alone. Pitch B shows similar properties to pitch A when sparged with a hydrogen containing gas. However, the use of an oxygen containing gas produces an increase in both TI fraction and in carbon yield. The two pitches have behaved very differently and this may help to explain contradictory results reported in the literature.

Hydrogen produces a chemical change in both pitches. The nature of this chemical change is probably a molecular growth mechanism which introduces bonds that are unable to survive the pyrolysis process.

With oxygen sparging pitch A shows no change relative to hydrogen sparging. Pitch B shows marked improvement in carbon yield and TI indicating that chemical changes are occurring of an oxidative nature which are producing enhanced levels of TI and are sufficiently stable to withstand pyrolysis and hence increase carbon yield.
Figure 97. Graph of $1/\text{sparge yield}$ vs. carbon yield for pitch A

Figure 98. Graph of $1/\text{sparge yield}$ vs. carbon yield for pitch B
Figure 99. Graph of 1/sparge yield vs. toluene insolubles for pitch A

Figure 100. Graph of 1/sparge yield vs. toluene insolubles for pitch B
4.9 Pitch $\Delta CY/\Delta SP$ Values

A quantity that has been used in the past [5] to assess the degree of improvement of a pitch for use in carbon-carbon composites, brought about by sparging the pitch, is the relative magnitude of change in carbon yield to the change in softening point i.e. the $\Delta CY/\Delta SP$ value. It is thought that a high increase in carbon yield is good and as low as possible increase in softening point is good (since pitches with lower softening points require less energy before they are very liquid and can impregnate into carbon fibres). Thus a high $\Delta CY/\Delta SP$ value is preferred. Table 17 below gives the $\Delta CY/\Delta SP$ values for all the modified pitches.

Table 17. $\Delta CY/\Delta SP$ values

<table>
<thead>
<tr>
<th>Pitch</th>
<th>$\Delta CY$</th>
<th>$\Delta SP$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH1</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>AH2</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>AH4</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>AO1</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>AO2</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>AO4</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>BH1</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>BH2</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>BH4</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>BO1</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>BO2</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>BO4</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

There is little, if any, difference between the $\Delta CY/\Delta SP$ values for the AH, AO and BH series of pitches but the BO series have $\Delta CY/\Delta SP$ values that are significantly higher. We now know that a chemical process is occurring for this series of pitches that is not occurring for the other three series of pitches and so it follows that this chemical process is responsible for the higher $\Delta CY/\Delta SP$ values in the BO pitches. This chemical process in pitches B treated with oxygen thus leads to an improvement in the pitch for use in carbon-carbon composites in terms of $\Delta CY/\Delta SP$ value.
4.10 The Composites

After having characterised the pitches the composites were fabricated. Figure 101 below is a photograph of the final composites. The composites were designated the same labels as the pitches that were used to make them. The dimensions of the composites were approximately 10 cm × 3 cm × 0.3 cm.

![Figure 101. Photograph of the series of 14 composites](image)

The composites were then characterised. The next sections give the results and discussion for the composite characteristics.
4.11 Composite Bulk Densities

This section discusses the bulk densities of the composites made from different pitches before and after impregnations as well as after each intermediate impregnation stage. The data for initial and final bulk densities is given in tables 18 and 19 below.

Table 18. Data for initial composite bulk densities

<table>
<thead>
<tr>
<th>Sparge time / hours</th>
<th>Initial bulk density / g cm$^{-3}$ ± 0.06 g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AH</td>
</tr>
<tr>
<td>0</td>
<td>0.84</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Table 19. Data for final composite bulk densities

<table>
<thead>
<tr>
<th>Sparge time / hours</th>
<th>Final bulk density / g cm$^{-3}$ ± 0.04 g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AH</td>
</tr>
<tr>
<td>0</td>
<td>1.07</td>
</tr>
<tr>
<td>1</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>1.29</td>
</tr>
<tr>
<td>4</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Figure 102 is a graph of initial bulk densities (before any impregnation stages) of the composites as a function of pitch sparge time. The initial bulk densities range from 0.84-1.12 g/cm$^3$. The density of raw pitch A was lower than that of pitch B. The density of the composite made from pitch A after 1 hour of sparging in both gases showed an increase from the raw pitch value but composites made from pitch B sparged for 1 hour did not increase in density from the composites made with untreated pitch.

The rest of the composites made from pitches sparged for 2 and 4 hours have very similar densities. Hence sparging the pitches for longer periods than 1 hour did
not increase initial composite density. Also the type of pitch and type of sparging atmosphere did not affect the initial bulk density with more than 1 hour of sparging.

Figure 103 is a graph of final bulk densities of the composites (after three impregnations) as a function of pitch sparge time. The final densities range from 1.27-1.38 g/cm$^3$. As for the initial bulk densities, the composite made from raw pitch B has a higher final bulk density than that made from raw pitch A. Pitches A treated for 1 hour with either sparge-gas have an increased final bulk density from the raw pitch (as they had an increased initial bulk density after 1 hour). Composites made from pitches B that have been sparged for 1 hour in either gas have decreased in density from the composites made from the raw pitch B. (The initial bulk densities of composites from pitches B sparged from 1 hour remained the same as the composite made from the raw pitch). For composites made from pitches that have been sparged for 2 or 4 hours, the composites made from pitches AH, AO, and BH show little change in density from the 1 hour sparged composites. The composite made from pitch BO has significantly decreased in final density after 4 hours. (This was not the case for initial densities). The fact that the composite made from BO has a lower final density than the other composites shows that this pitch has been modified differently to give a lower density carbon in the composite than the others. This also fits the theory of pitch BO having undergone different reaction processes than the other pitches. These reactions have caused this undesirable lower final bulk density in the composite made from BO.

The trends for initial and final bulk densities are the same for composites made from pitches that have been sparged for 0, 1 or 2 hours. This proves that all the pitches that have been sparged for 0, 1 or 2 hours impregnate in the same way as each other. The trends for initial and final bulk densities for composites that have been made with pitches that have been sparged for 4 hours are the same for pitches AH, AO and BH but different for the composite made from BO. This shows that pitch BO impregnates in a different way from all the other pitches i.e. BO does not impregnate as efficiently as the other 4 hour-sparged pitches. This fits in with the theory that pitch BO has undergone different chemical reactions to the other pitches and these reactions have caused pitch BO to be a less efficient impregnant.
Figure 102. Graph of initial bulk density of composite vs. sparge time

Figure 103. Graph of final bulk density of composite vs. sparge time
Figures 104-108 are graphs of the bulk density of composites as a function of the number of impregnations from 0-3. The error bars on these graphs are quite large but it can be seen that in most cases the density of the composite increased with each successive impregnation. The apparent decrease in density after impregnations of a few samples is explained either by the fact that bits of sample had chipped off thus causing a decrease in the measured mass and thus a decrease in measured density or simply that the value’s error makes it seem like a decrease has occurred when in fact it may have stayed the same or even increased.

The increases in density after each impregnation stage are quite similar to each other and table 20 below shows the actual values of change in density of the composites after each impregnation.

Table 20. Density changes after each impregnation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density change after impregnation</th>
<th>Density change after impregnation</th>
<th>Density change after impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>A</td>
<td>0.03</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>AH1</td>
<td>-0.12</td>
<td>0.16</td>
<td>0.00</td>
</tr>
<tr>
<td>AH2</td>
<td>0.00</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>AH4</td>
<td>-0.04</td>
<td>0.27</td>
<td>0.12</td>
</tr>
<tr>
<td>AO1</td>
<td>-0.07</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>AO2</td>
<td>-0.01</td>
<td>0.07</td>
<td>0.28</td>
</tr>
<tr>
<td>AO4</td>
<td>0.03</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>B</td>
<td>0.15</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>BH1</td>
<td>0.15</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>BH2</td>
<td>0.12</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>BH4</td>
<td>0.10</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>BO1</td>
<td>0.17</td>
<td>-0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>BO2</td>
<td>-0.14</td>
<td>0.23</td>
<td>0.06</td>
</tr>
<tr>
<td>BO4</td>
<td>-0.06</td>
<td>-0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>mean value</td>
<td>0.02</td>
<td>0.11</td>
<td>0.08</td>
</tr>
</tbody>
</table>

From this table it can be seen that the increases in density after the first impregnation were smaller than those after the next two impregnations. This is because in the first impregnation the sample and pitch impregnant were only heated up to 250°C whereas for impregnations 2 and 3 the maximum impregnation temperature reached was 350°C, as described in section 3.5. The higher temperature caused a decrease in viscosity such that more pitch was able to filter into the pores of the composites.
In general, impregnation 3 did not lead to such high increases in density as impregnation 2 suggesting that successive impregnations, at the same conditions as impregnation 2, will result in lower and lower increases in density. This is probably due to the closing off and narrowing of pores after each impregnation which prevents pitch entering the pore structure.

It can be seen from graphs 104-108 that the increases in density after each impregnation for all the different pitches were quite similar to each other which shows that all the pitches except BO impregnated in the same way and explains why the graphs for initial and final densities vs. sparge time showed similar trends as each other.

Figure 104 shows that the density of composites made using raw pitch B are higher than those of composites made using raw pitch A at every impregnation stage. Thus it would seem better to use pitch B if a higher density composite is required.

Figure 105 shows the densities for all composites made from pitches originating from pitch A. The densities of the composites made from treated pitches are slightly set above the composite made from untreated pitch. There is no significant difference between the densities of the composites made from pitches sparged by different gases at any stage of impregnation. So sparging has improved the composite densities from composite made using raw pitch but as already proved from graph 102, but the improvement ceased after 1 hour of sparging. The densities were independent of the type of sparge gas used for pitch A. These results fit very well with the theory that sparging pitch A involves chemical changes but that the changes are independent of sparge gas.

Figure 106 shows the densities for all composites made from pitches originating from pitch B. In this case the densities of the composites made from pitch sparged with hydrogen are higher than those made from pitch sparged with oxygen. This did not show up very well in the graphs of initial and final densities but can be seen clearly here. Again, this fits with the theory that pitch B undergoes different chemical changes with the different sparge gases. The composites made from oxygen sparged pitches have been shown to have higher carbon yields and ΔCY/ΔSP values than one made from H-sparged pitches but surprisingly these improvements are at the expense of composite density. It is possible that the molecular growth mechanism,
that improves the carbon yield, has also increased the melt viscosity and therefore reduced the efficiency of the infiltration process.

Figure 107 shows the densities for all composites made from pitches that have been sparged with hydrogen. It can be seen that the composites made from pitches originating from B have higher densities than those from pitches originating from A. This is the same result as for the composites made from the raw pitches in figure 102. This indicates that hydrogen sparging affects the two pitches in the same way.

Figure 108 shows the densities for all composites made from pitches that have been sparged with oxygen. This time the composites made from the two pitches have similar densities to each other. Since the composite made from raw pitch A started with a lower density than that made with pitch B it follows that the oxygen sparging has had a different affect on the two pitches, causing pitch A to increase its density more than pitch B. Hence the different reactions that have been proved to be occurring in pitch B due to oxygen sparging result in B having lower increases in density composites than A, even though the CY and ΔCY/ΔSP values have increased more for pitch B treated with oxygen.
Figure 104. Graph of composite density vs. number of impregnation cycles for raw pitches A and B
Figure 105. Graph of composite density vs. number of impregnation cycles for pitches originating from pitch A

Figure 106. Graph of composite density vs. number of impregnation cycles for pitches originating from pitch B
Figure 107. Graph of composite density vs. number of impregnation cycles for hydrogen sparged pitches

Figure 108. Graph of composite density vs. number of impregnation cycles for oxygen sparged pitches
4.12 Composite True Densities

The true densities were found using powdered samples and helium pycnometry. The data for the final true densities of the composites is given in table 21 below. The errors in this graph are smaller from those in the bulk density graphs and so should show any trends if they exist. The true densities of the composites range from 1.727-1.771 g/cm$^3$ compared to the bulk densities of 1.27-1.38 g/cm$^3$.

Table 21. Data for final true composite densities

<table>
<thead>
<tr>
<th>Sparge time / hours</th>
<th>Final true composite density / g cm$^{-3}$ ± 0.004 g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>AH 1.760, AO 1.760, BH 1.762, BO 1.762</td>
</tr>
<tr>
<td>1</td>
<td>1.768, 1.762, 1.771, 1.749</td>
</tr>
<tr>
<td>2</td>
<td>1.769, 1.756, 1.763, 1.7611</td>
</tr>
<tr>
<td>4</td>
<td>1.765, 1.733, 1.745, 1.727</td>
</tr>
</tbody>
</table>

Figure 109 is a graph of the final true densities of composites vs. pitch sparge time. The graphs look similar to the final bulk density graph between 0 and 2 hours i.e. there is no real pattern. The composites show little change in density for pitches sparged for 0, 1 or 2 hours and the densities of all the composites are similar to each other. These findings reinforce the conclusions drawn from the bulk density graph that all pitches treated for up to 2 hours give composites with very similar densities.

However, between 2 and 4 hours of pitch sparge time, the final true density graphs are different to the final bulk density graphs. Between 2-4 hours the true densities of the composites all decrease whereas the bulk densities showed little change except for B40 which had decreased. So, sparging any of the pitches for 4 hours affects the true densities of the composites made from them. Since the true density is affected by sparging between 2-4 hours and bulk density is not, this means that the intrinsic structure of the carbon in the composite must have been modified, and not just the composite pore structure. Sparging the pitch for 4 hours modifies the pitch and thus the final carbon structure of the composite in a negative way so as to decrease composite density. The decreases in true density of the oxygen-treated
pitches, after 4 hours, show slightly larger decreases than the hydrogen-treated ones. This could indicate that the oxygen that was taken up by the pitch is released during carbonisation to form micropores within the matrix. These micropores are too small to be exposed when grinding and therefore result in a low value for true density.

Since composites made from all four pitch / sparge-gas combinations show this decrease in density, it must be due to chemical reactions caused by both gases and affecting both pitches or, indeed, is just a thermal effect. The largest decrease in composite density is undergone by pitch B treated with oxygen. The reaction processes occurring in this pitch / sparge-gas combination are different to those in all the others and this could be the explanation for the larger decrease in true density in pitch B treated with oxygen.

4.13 Total composite porosities

The total porosities of the composites range from 24.1-30.5%. The data for the total composite porosities is given in table 22 below.

Table 22. Data for total composite porosities

<table>
<thead>
<tr>
<th>Pitch sparge time / hours</th>
<th>Total composite porosity / % ± 0.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AH</td>
</tr>
<tr>
<td>0</td>
<td>26.5</td>
</tr>
<tr>
<td>1</td>
<td>28.7</td>
</tr>
<tr>
<td>2</td>
<td>26.3</td>
</tr>
<tr>
<td>4</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Figure 110 is a graph of total composite porosity vs. pitch sparge time. The composite made from raw pitch A had a higher porosity than that made from raw pitch B. (The composite made from raw pitch A had a lower bulk density than that from pitch A).

The only pattern evident in this graph is that the composites made from pitch B sparged in oxygen always have higher porosities than those made from pitch B treated in hydrogen. This again illustrates the different chemical reactions occurring
in this pitch with oxygen and hydrogen. This reaction can now be said to account for a higher total porosity in composites made from pitches B treated with oxygen compared to pitches B treated with hydrogen.

Sample BO4 has a comparable total porosity to the other samples but has a lower bulk density of 0.92 g/cm\(^3\) than the other samples. This is probably due to the presence of microporosity in this sample that has been discussed in section 4.12.
Figure 109. Graph of final true composite density vs. pitch sparge time

Figure 110. Graph of total composite porosity vs. pitch sparge time
4.14 Open and Closed Composite Porosities

The open porosities range from 21.6-27.9% and the closed porosities range from 2.1-3.4%. Table 23 below gives the data for the open and closed porosities of the composites.

Table 23. Data for open and closed composite porosities

<table>
<thead>
<tr>
<th>Sample</th>
<th>Open porosity / % ±0.2%</th>
<th>Closed porosity / % ±0.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>23.8</td>
<td>2.7</td>
</tr>
<tr>
<td>AH1</td>
<td>26.4</td>
<td>2.3</td>
</tr>
<tr>
<td>AH2</td>
<td>23.6</td>
<td>2.7</td>
</tr>
<tr>
<td>AH4</td>
<td>25.4</td>
<td>2.1</td>
</tr>
<tr>
<td>AO1</td>
<td>21.8</td>
<td>2.9</td>
</tr>
<tr>
<td>AO2</td>
<td>24.5</td>
<td>2.6</td>
</tr>
<tr>
<td>AO4</td>
<td>22.1</td>
<td>3.4</td>
</tr>
<tr>
<td>B</td>
<td>22.5</td>
<td>2.5</td>
</tr>
<tr>
<td>BH1</td>
<td>21.9</td>
<td>2.8</td>
</tr>
<tr>
<td>BH2</td>
<td>21.6</td>
<td>3.1</td>
</tr>
<tr>
<td>BH4</td>
<td>23.8</td>
<td>3.2</td>
</tr>
<tr>
<td>BO1</td>
<td>22.9</td>
<td>3.1</td>
</tr>
<tr>
<td>BO2</td>
<td>27.9</td>
<td>2.6</td>
</tr>
<tr>
<td>BO4</td>
<td>23.7</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Figures 111 and 112 show the open and closed porosities of the composites versus the pitch sparge time. It is evident that the majority of pores in all the composites are open pores.

The open porosity graphs follow the same trends as the total porosity graphs and so all arguments follow through. The closed porosities are all very close to each other within their error. The composite made with pitch A treated with hydrogen has a slightly lower closed porosity than the other pitches after 4 hours of pitch sparging.
Figure 111. Graph of composite open porosity vs. pitch sparge time

Figure 112. Graph of composite closed porosity vs. pitch sparge time
4.15 Optical Microscopy of the Composites.

Optical micrographs of every composite were taken: one to show the fibres in transverse section, one to show the fibres in longitudinal section and several to show the typical pore structure of each composite. In this section selected micrographs of the pore structures of the composites are included to illustrate the conclusions that have been reached about the composite porosities.

The first conclusion that has been reached so far about porosity are that raw pitch A has a higher total porosity than raw pitch B. The micrographs in figure 113 illustrate this point. The composite made from A (figure 113 (a)) has a higher occurrence of pores than the one made from pitch B (figure 113 (b)). Also the pores in the composite made from pitch A are larger than those in the composite made from pitch B.

The second conclusion about porosity is that the total porosity of the composites made from pitch BO are higher than the porosity of the composites made from BH. This is illustrated in figure 114. The micrograph of BO2 (figure 114(a)) contains more pores than the micrograph of BH2 (figure 114(b)).

The third conclusion about porosity was that the porosity in all the composites is mainly open porosity. It is impossible to ascertain from a micrograph whether a pore is open or closed as the cracks or vacancies leading away from the pore may not be in the same plane as the micrograph. However, the pore marked, P in figure 113 (a) clearly has a small crack leading away from it on the right hand side.
Figure 113. Optical micrographs showing typical porosity in (a) Composite made from pitch A, (b) composite made from pitch B.
Figure 114. Optical micrographs showing typical porosity in (a) composite made from pitch BO2, (b) composite made from pitch BH2.
4.16 Mechanical Properties of the Composites

As was explained in section 3.9 it was initially intended to find the inter-laminar shear strength of the composites but it occurred that all the samples failed by brittle fracture and so it was decided to use the data for flexural strength and modulus determination. The data for flexural strength and modulus of the composites is given in table 24 below. The errors are quite large for both properties due to the fact that this type of mechanical testing requires numerous samples for accurate results and only 9 samples were available for each test. This requirement for a large number of test samples is due to the wide variation between sample structures in terms of cracks and pores and the wide variation in the way the samples fail. This is particularly true for brittle materials where the fracture mechanisms are flaw dependent.

Table 24. Data for flexural strength and modulus of the composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural strength of composite / MPa ± 69 MPa</th>
<th>Flexural modulus of composite / GPa ± 29 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>598</td>
<td>139</td>
</tr>
<tr>
<td>AH1</td>
<td>452</td>
<td>133</td>
</tr>
<tr>
<td>AH2</td>
<td>568</td>
<td>136</td>
</tr>
<tr>
<td>AH4</td>
<td>556</td>
<td>104</td>
</tr>
<tr>
<td>AO1</td>
<td>559</td>
<td>211</td>
</tr>
<tr>
<td>AO2</td>
<td>538</td>
<td>186</td>
</tr>
<tr>
<td>AO4</td>
<td>569</td>
<td>223</td>
</tr>
<tr>
<td>B</td>
<td>521</td>
<td>79</td>
</tr>
<tr>
<td>BH1</td>
<td>555</td>
<td>90</td>
</tr>
<tr>
<td>BH2</td>
<td>552</td>
<td>123</td>
</tr>
<tr>
<td>BH4</td>
<td>542</td>
<td>177</td>
</tr>
<tr>
<td>BO1</td>
<td>588</td>
<td>145</td>
</tr>
<tr>
<td>BO2</td>
<td>486</td>
<td>140</td>
</tr>
<tr>
<td>BO4</td>
<td>335</td>
<td>88</td>
</tr>
</tbody>
</table>
4.16.1 Flexural strength

The flexural strengths of the composites range from 335-599 MPa. Figure 115 is a graph of flexural strength of composite versus the pitch sparge time of the pitch used to make the composite.

The flexural strengths of the composites made from pitches AH, AO, and BH show no change, within error, as the pitch sparging time increase. The values of flexural strength for these three pitches are also the same as each other, within error. This indicates that sparging the pitches has no affect on the flexural strength of these composites.

The flexural strength of the composite made from pitch BO decreases as the sparge time of the pitch increases. It has been shown that oxygen-sparged pitch B undergoes some kind of chemical process that is different from any chemical changes in the other three types of pitch/treatment combination. The undesirable decrease in flexural strength of the composites made from BO, which does not occur for the other pitches, is probably a result in the change in chemical structure of pitch BO which has not occurred in the other pitches.

It seems that pitch B treated with oxygen has an increased carbon yield at the expense of flexural strength. A deterioration in mechanical properties with increasing carbon yield is well reported in the literature [1].

4.15.2 Flexural modulus

The flexural moduli of the composites range from 79-223 GPa. Figure 116 is a graph of flexural modulus of composite versus the pitch sparge time of the pitch used to make the composite. The composites made from the raw pitches, A and B, have similar flexural moduli as each other, within error. The flexural moduli of composites made from pitches AH and BO show no change, within error, as pitch-sparging progresses and are indeed the same as each other, within error. The flexural moduli of composites made from pitches AO and BH increase as pitch sparge time increases. These trends do not fit in with the chemical processes that are occurring. The increases in pitches AO and BH are probably either anomalous results or, result from
thermal structural changes that happened to take place for these two pitches but not the other two.
Figure 115. Graph of composite flexural strength vs. pitch sparge time

Figure 116. Graph of composite flexural modulus vs. pitch sparge time
5 CONCLUSIONS

The first part of this project examined the characteristics of a set of pitches that had been produced by sparging in a hydrogen or oxygen atmosphere for different periods of time. The conclusions for this part of the work are given here:

1. All properties of all pitches (softening point, carbon yield and insoluble fractions) showed marked increases after 1 hour of sparging and smaller changes after 2 and 4 hours (with the exception of quinoline insolubles).

2. After modelling the pitch sparging process and fitting the experimental data to the model it was concluded that pitches A and B behaved differently during sparging. This was not surprising since the two pitches had been shown to have different compositions by a number of methods. For example, pitch B was found to contain coke particles whereas pitch A did not. Pitch B had higher percentage sparge yield than pitch B indicating a higher average molecular weight and pitch B had a higher percentage of insolubles than A in pentane, toluene and quinoline.

3. Pitch A behaved in the same way whether it was sparged with a hydrogen- or an oxygen-containing gas. Sparging pitch A with either gas was shown to produce chemical reactions that enhanced the amount of toluene insoluble material present. This material did not withstand pyrolysis and thus did not enhance the carbon yields of the pitches. Since sparging with both gases produced these reactions in pitch A it was concluded that the reactions were probably thermally induced.

4. Pitch B was found to behave very differently after sparging with the different gases. After sparging with hydrogen pitch B showed similar results to pitch A. However, after sparging pitch B with oxygen there was a larger increase in toluene insoluble material and this correlated with a larger increase in carbon yield. It was concluded that a different chemical process was occurring in this case which produced an enhanced amount of toluene insoluble material. This material was able to withstand pyrolysis and hence increased the carbon yield. The type of reaction that was occurring was predicted to be either an oxidative molecular
growth or a decrease in volatility of polyaromatics brought about by the addition of oxygen functionality.

The conclusion that pitch B treated with oxygen undergoes different chemical reactions to the other pitch / treatment combinations is backed up by the trends seen in many of the pitch properties:

• The softening point of the hydrogen sparged pitches derived from pitch B were always higher than the oxygen sparged pitches derived from pitch B.
• The carbon yields: The gas that gave the highest carbon yield was dependant on which pitch, A or B, was being used.
• The $\Delta CY/\Delta SP$ values for the pitches in the BO series were markedly higher than those of any other series of pitches.

In the second part of this work the composites that had been fabricated from the set of 14 pitches were characterised. The conclusions for the second part of the project are given here:

5. It was found that the composite characteristics correlated closely with their constituent pitch characteristics, especially in the fact that the characteristics of the BO composites were markedly different from all the others. It was concluded that the reason for any characteristics that were notably different for pitches BO was that the reactions that occurred in these pitches were different to those that occurred in the other pitches. The characteristics that were markedly different for pitch BO are given here:

a. The final bulk density of BO is showed a significant decrease after 4 hours whereas the other composites showed little change after 4 hours

b. Pitch BO impregnated less efficiently than all the other pitches after 4 hours. This was found by comparing the trends for initial and final bulk densities and looking
at the gradients of the density versus impregnation number graphs. Pitches AH, AO and BH all impregnated with comparable efficiency.

c. The increases in bulk density of pitch B sparged in oxygen was lower than pitch B sparged in hydrogen. (The increase in bulk density of pitch A were similar when it was sparged in hydrogen and oxygen)

d. The true density of BO after 4 hours had decreased significantly more than the other composites. (Sparging for 0, 1 or 2 hours lead to no change in true density of any of the composites and there was no difference between true density of the composites.)

e. The total porosities of BO were found to be greater than those for BH. (The porosity in all the composites was mainly open. The open porosities showed the same result as the total porosities. The closed porosities of the composites showed no pattern.)

f. The flexural strength of BO compared to the other composites was lowered, especially after 4 hours of sparging. (The flexural modulus was not affected by the reactions in pitches BO.)

In summary, the chemical reactions that occurred in the preparation of pitch BO lead to pitches with increased TI content, increased carbon yield, increased softening points and increased ΔCY/ΔSP values. These are all advantageous changes if the pitches are to be used to fabricate composites.

The reactions in the preparation of pitch BO lead to composites with lower final bulk densities, lower bulk densities after each impregnation, lower efficiency of impregnation of the pitch, lower true densities, higher total porosities and reduced flexural strength. These are all unfavourable changes if the pitch is to be used to fabricate composites.
6 RECOMMENDATIONS FOR FUTURE WORK

1. In this work it was found that two different pitches behaved very differently under sparging. All that is known about the different compositions of pitch A and B are that pitch B contains more pentane insolubles, toluene insolubles, quinoline insolubles than pitch A and that pitch B contains coke particles that are absent in pitch A. It would be useful to obtain a number of pitches, find out in detail the composition of the pitches, and relate the composition to the effect of sparging on the pitch.

2. In this work re-impregnation stages were carried out in a crude manner with a small amount of pitch in a boiling tube and a vacuum. It would be useful to use a larger vessel with a larger amount of pitch. It would be advantageous if the container was metallic so that the heat is conducted more efficiently to the pitch. Finally, the impregnations would be more effective if a positive pressure was applied to the pitch and composite as in HIPIC.

3. The composites in this work were made using carbon fibre cloth that was coated in potassium nitrate in order to promote thermosetting in the pitch and prevent pitch run out during press moulding. It was found that the composites that resulted exhibited unusually strong fibre matrix bonding such that they did not behave as composites. It would be useful to experiment with different carbon fibre cloth, different coating and indeed different press-moulding techniques in order to fabricate composites that had enough bonding between fibre and matrix to maintain the structure of the composite, but not too much bonding such that the material does not behave as a composite. Ideally a press mould that could be heated to 500°C without pitch run out is required in order to permit composite production without the use of potassium nitrate.

4. It would be useful to examine the carbon yields of the composites themselves (before carbonisation). In this work the carbon yields of the sparged pitches were
determined and this gives an indication of the composite carbon yield but it would be useful to find the carbon yield of the composite itself after the press-mould stage and after each successive impregnation.

5. Much more work could be done on the mechanical properties of these series of pitches. If composites were made that did not break by brittle fracture then the true composite properties could be determined, including inter-laminar shear strength.

6. More work on the microstructures of these composites could be done using techniques such as SEM, TEM, x-ray and electron diffraction. The microstructures could be related to the pitch type used in their manufacture.

7. It would be useful to determine the porosities of the composites using mercury intrusion porosimetry to give a more realistic idea of how open or closed the pore structure is in terms of more pitch being able to infiltrate the pores.
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APPENDIX A

Paper to be published

Properties of Gas Sparged Coal Tar Pitch Compositions

S. F. Myram, J. W. Patrick and M. C. Turpin

Dept. of Chemical Engineering

Loughborough University, Loughborough, Leics., LE11 3TU, UK.

Abstract

Two pitches have been modified to varying degrees by gas sparging at 400°C for various times. The process gas used was either 1% oxygen in nitrogen or 5% hydrogen in nitrogen. Results indicate that for pitch A, the product is independent of sparge gas and that sparging does not benefit the carbon yield with respect to the raw pitch. Some improvement in toluene insoluble content is observed, however, it would appear that this does not translate to the formation of additional carbon. Overall, the results indicate that the predominant reaction giving rise to the hardening of the pitch is stripping of volatile matter. Pitch B shows different behaviour, whilst with the hydrogen sparge gas the results are similar to pitch A, the oxygen sparge gas shows marked improvement in the yield of carbon from the raw pitch. The improvement in pitch B with oxygen is presumably due either to an oxidative molecular growth mechanism or to the incorporation of oxygen functionality into the pitch and a consequential reduction in volatility.

Keywords: A. Coal Tar Pitch, B. Heat-Treatment.
1. Introduction

Coal tar pitches have long been used as carbon precursors, mainly in the form of a binder phase in electrodes and refractory compositions. One of the techniques widely practised for the modification of pitch properties is air blowing or gas sparging. In this technique the pitch is heated in an enclosed vessel whilst air or other gas is passed through the pitch from the base of the container. The pitch softening point and carbon yield are both elevated by this procedure [1]. For many applications such changes in the pitch properties are considered highly beneficial.

Coal tar pitches are complex mixtures of various chemical species. The material is highly carbonaceous with the majority of carbon (≈90%) existing in an aromatic environment [2]. Molecular weights of the molecular species present vary between approximately 300 to in excess of 10000 [3, 4]. The preferred model of pitch is thus one of large aromatic and polycyclic aromatic species bearing occasional aliphatic side chains. Analysis of pitches using techniques such as HPLC [5] can identify individual components of pitch, but also indicate that the material is composed of a wide range of molecular species and contains many and various functional groups [6]. The diversity of species present in pitches makes interpretation of pitch hardening processes, such as gas sparging, rather complex, and the question of what effect the gas sparging process has on the chemical nature of the pitch has never been satisfactorily answered.

In general the gas sparging process is believed to harden the pitch by two distinct mechanisms [1]. The first of these simply involves the volatilisation of the lighter fractions in the pitch, which is hardened by the loss of the plasticizing properties of these species. The second mechanism involves the condensation of molecular species
in the pitch, forming a progressively heavier fraction of consequentially reduced volatility and improved carbon yield. The second mechanism may also operate by two distinct mechanisms. In the first, the pitch may simply exhibit a thermal polymerisation [7], perhaps aided by the stirring action of the passing gas. Whilst in the second, the passing gas may be chemically reactive towards the pitch and that reactivity may result in chemical hardening.

The role of oxygen in the air sparged processing of pitch is unclear, the most obvious possibility is that the oxygen results in molecular growth either via the introduction of ether cross-linkages, or alternatively via an oxidative dehydrogenation reaction, leading to the formation of new carbon-carbon bonds [8, 9, 10]. Diffuse reflectance FTIR (DRIFT) studies of gas sparged pitches[1] are reported to show little evidence of oxidation, a result which is interpreted in terms of a dehydrogenation condensation process. However, similar measurements on mesophase pitches [11, 12], indicate that prolonged oxidation results in the introduction of etheric, carboxylic and carbonyl groups. It is uncertain at present whether gas sparging with air results in an oxidative process and if so what that process might be.

An alternative mechanism, which does not involve molecular growth, for the hardening of pitches by air sparging, may be that the pitch picks up significant oxygen functionality and is hardened by the reduction in volatility which normally accompanies the introduction of molecular polarity.

In this paper, the effect of gas sparging on two coal tar pitches is assessed in terms of the changes in physical properties of the product pitches. The effect of oxygen on the gas sparging process is assessed by variation of the process gas, from a simple mixture of oxygen and nitrogen through to a mixture of hydrogen in nitrogen. This
change over from an oxidising gas to a reducing gas, should help to elucidate particular hardening effects associated with oxygen. Alternatively, if the sparging process is merely a stripping reaction, in which the process gas is simply a vehicle for volatile removal, then the results will be independent of the process gas used.

2. Experimental

2.1 Samples studied

All the gas sparged pitches produced and studied in this work were prepared from two precursor coal tar pitches. Selected properties of the two pitches are tabulated in Table 1.

The pitches are supplied from different manufacturers and are both prepared on a commercial basis.

The low quinoline insoluble content of pitch A, results from hot filtering to remove coke particles.

2.2 Gas sparge reactor

The gas sparge reactor used to produce the sparged pitches was of a tubular design, produced entirely in Inconel 601. The use of an expensive nickel alloy was shown to be necessary by initial work using 316 stainless which showed considerable embrittlement, either due to hydrogen dissolution or carbide precipitation at the grain boundaries and ultimately leading to catastrophic failure.

The system used is shown schematically in Figure 1. Incoming gas is heated in the process gas pre-heater prior to injection through a 16 μm sintered nickel frit. The tubular reaction is heated by two independently controlled heater bands each
delivering a peak power of 2kW. The use of dual heater bands was necessary to accommodate the considerable difference in thermal mass between the upper and lower regions of the reactor. After passage through the liquefied pitch, the gas passes over the baffle system in the upper half of the reactor vessel, this being designed to prevent pitch carry-over with the volatile phase. Exhaust gases are passed through a particulate bed with particle size gradation to trap the fine aerosol precipitate of volatile matter. The three heated zones of the reactor system (i.e. pre-heater and two vessel heaters) were independently controlled using Eurotherm 91e PID controllers. In use this allowed the baffles to be operated at a slightly higher temperature than the rest of the reactor, thereby reducing the tendency for volatilised species to reflux back into the reaction vessel. Gas inlets to the system are supplied via calibrated flow meters, to ensure accurate sparge gas composition and flow rate.

2.3. Process Conditions

The gas sparged reactor is charged with 300g of the pitch under study and the flange ends bolted down onto high temperature sealant gaskets. Gas flow is introduced into the reactor at a rate of 5 litres per minute, the gas being either 1% oxygen in nitrogen or 5% hydrogen in nitrogen. The vessel heaters are energised and the vessel temperature raised to 400°C over the course of approximately 40 minutes. The vessel is maintained at temperature for 1, 2 or 4 hours before the heaters are de-energised and the reactor allowed to free cool to room temperature. The resolidified pitch is recovered from the vessel and the approximate weight determined, in this way a percentage yield for the sparging process may be estimated.
2.4 Pitch Characterisation

2.4.1 Softening Point

A small piece of the pitch under study was placed into a shallow 6.25 mm hole machined into the surface of a copper block. The block was heated externally at a rate of 3°C/min whilst the block temperature was monitored by a thermocouple inserted into a separate channel beneath the sample well. The sample was observed closely during heating and the temperature at which the sharp angular facets of the pitch fracture surface begin to lose definition, due to flow, was noted. The measurement was repeated twice for each pitch to ensure reproducibility. The use of this non-standard method was considered preferable to the established ring and ball measurement since the quantities of pitch available from each gas sparge run were small. Comparison of the measured data with R&B measurements on the untreated pitches show good agreement to within 5°C. Reproduction of the method 6 times on a single pitch indicates that the precision of the average of 2 measurements is ±6°C which is comparable to the R&B method.

2.4.2 Carbon Yield

250mg of the pitch was carbonised in a Cahn TGA system. The sample was placed in a small ceramic crucible suspended from the TGA microbalance and maintained with a nitrogen atmosphere. The sample was heated to 1100°C, at a linear heating rate of 3°C/min, with a 60 minute hold at temperature before cooling at a similar rate. Carbon yield was determined from the relative masses of the pitch precursor and the carbon residuum.
2.4.3 Solubility

Pitch solubilities were determined by a modified ASTM method [13]. One gram of pitch (<212μm) was placed in a 100ml round bottomed flask together with 50ml of the solvent under study. Pentane and toluene mixtures were refluxed for 20 minutes, whilst quinoline mixtures were maintained at 85°C in a water bath for a similar period. Samples were continuously agitated during this time.

Pentane samples were hot filtered through a No.4 Gooch crucible, whilst other solvents were filtered after cooling to exactly 50°C. Accurate temperature control was found to be necessary as the toluene solubility appears to be strongly temperature dependent.

Insolubles were washed with 3 x 10ml aliquots of the solvents under study before drying overnight at a temperature 10°C above the solvents boiling point. Quinoline insolubles were of necessity dried at 100°C as the boiling point of quinoline is above the softening point of the pitch studied.

The yield of insoluble material was determined by weight.

2.4.4 Optical Microscopy

Samples of the sparged pitches were mounted in an epoxy resin for micrographical examination. The samples were plain ground and polished to a 1μm finish. Microscopy was conducted using a xenon light source and crossed polarisers with a 1λ tint plate. The objective of this exercise was to identify the formation of anisotropic material during the sparging process.
3. Results and discussion

3.1 Sparge reactor yields

Yields from the gas sparge reactor are obviously approximate as it is impossible to account for all mechanical losses in unloading the reactor. The results show yields in the range of 50 to 75% by weight. It is generally the case that longer sparge times result in lower yields, this is to be expected if the evolution of volatile matter continues throughout the sparging process. Yields from pitch B are higher than for pitch A, a fact which may be indicative of the higher softening point in pitch B being due to a higher average molecular weight. The full data for pitch yield from the sparge reactor is shown in Table 2.

3.2 Pitch properties

Pitch properties are tabulated in Table 3. Standard errors for all measured parameters were determined by a six-fold repeat measurement on a single sample of pitch. In general the error margins of the measured parameters are small. Batch to batch errors have also been assessed, by a four-fold duplication of the Pitch B datum with 2 hour hydrogen sparging. This datum was chosen, as experience showed that the 2 hour data exhibited the highest variability of the 3 time periods studied, the choice of pitch and process gas was arbitrary. Batch to batch variability of each parameter is tabulated in the footing of Table 3.

Micrographical examination showed that none of the samples had developed mesophasic character during processing, although some anisotropic coke inclusions were noticeable in pitch B.
It is apparent that batch to batch variability for the processing of pitches by this method is large. The reason for this is that the control of the process reactor is necessarily poor. The reactor can only be heated up to working temperature with the gas flow on, since otherwise the molten pitch will run through the sparge plate. This means that each batch receives a variable process time including approx. 40 minutes warming up and up to 90 minutes cooling down. Because these times are long relative to the process times used, the batch variability is bound to be large. The large batch to batch variability of the process is the reason for the occasionally anomalous entries in the tabulated data.

That said, the batch to batch variation is unimportant from the standpoint of the present work. Our primary interest is to create a range of pitches having different degrees of thermal treatment and to that end the process is successful.

Analysis of the measured data requires a postulate as to the mechanism by which pitch is hardened in the gas sparging process. The simplest model is one in which the pitch consists of two fractions, one of which comprises molecules which produce carbon on pyrolysis, the other being molecules which are volatile and evaporate during pyrolysis.

Let $W_c$ be the weight fraction of carbon producing molecules and $W_v$ the weight fraction of volatile molecules. Let the carbon yield, expressed as a weight fraction, obtained on pyrolysis of the raw pitch be $C$, and that of the gas sparged pitch be $C'$.

Relatively straightforward treatment of the model system yields:

$$C = \frac{\nu_c \cdot W_c}{W_c + W_v} = \nu_c \cdot W_c \quad (1)$$
Where \( \nu_c \) is the weight fraction of the carbon obtained from the carbon producing phase.

For the gas sparged pitch

\[
C' = \frac{\nu_c \cdot W_c}{W_c + W_v - W_l} = \frac{\nu_c \cdot W_c}{1 - W_l}
\]  (2)

Where \( W_l \) is the fraction weight loss of the pitch during sparging, i.e. \( 1-W_l \) is the sparge product yield.

Substitution of 1 into 2 yields by rearrangement:-

\[
\frac{1}{1 - W_l} = \frac{C'}{C}
\]  (3)

A plot therefore of the reciprocal sparge yield vs. the carbon yield of the gas sparged pitches should yield a straight line of gradient \( 1/C \), the carbon yield of the raw pitch. Moreover both the hydrogen and oxygen treated pitches should fall upon the same line, since in this simple model we have assumed that the process gas is non-reactive.

Conducting this exercise for Pitch A yields the data in Figure 2. It is clear that both sets of data do indeed fall upon the same line which has a correlation coefficient \( (r^2) \) of 0.97. The carbon yield for the raw pitch is estimated from the gradient at 28.3 % which is a tolerable agreement with the observed TGA value of 36.3%. The fact that the observed value of the raw pitch carbon yield is higher than the apparent value, determined from the plot, is satisfactory, since the observed value is obtained from
TGA under quiescent conditions and should be higher that observed if the pyrolysis was conducted in a gas sparged system.

Conducting the same exercise with pitch B gives markedly different results. It is clear from Figure 3 that for this pitch the results of sparging with hydrogen and oxygen containing gases are different. The hydrogen sparge data gives an apparent carbon yield for the raw pitch of 31% (correlation 0.977) which again is somewhat lower than the value observed in the quiescent TGA experiment. Once again it would seem that the carbon producing phase in pitch B is unchanged by the passage of hydrogen.

For the oxygen data it is apparent that much higher carbon yields are obtained than would be expected. The apparent carbon yield, obtained from the slope of the graph is 45% (correlation 0.995), significantly higher than the value obtained experimentally. The conclusion from this is that the oxygen containing process gas has chemically altered the pitch, to increase the quantity of the carbon producing phase at the expense of the volatile matter.

The findings from this analysis are in agreement with those obtained by the method of Fernandez et al [1] who use the relative magnitude of the change in carbon yield to the change in softening point as an indication of the degree of improvement in pitch carbon yield wrought by gas sparging. The term $\Delta CY/\Delta SP$ is included in Table 3 for comparative purposes. It is clear that pitch B with oxygen sparging gives the highest values of this parameter.

Extending this analysis further, it is clearly possible to substitute solvent insolubles data into the place of carbon yield and generate information regarding changes in the chemical nature of the pitch. Unfortunately, the PI and QI data presented in Table 3 can be seen to exhibit a small span of values measured with relatively low precision.
The TI data is much more amenable to analysis. Recasting equation 2 in terms of the TI data gives

\[
\frac{1}{1 - \frac{W_i}{W_I}} = \frac{\text{TI'}}{\text{TI}} 
\]

(4)

Where TI’ is the toluene insoluble fraction of a sample produced with a sparge reactor yield of \(1 - W_i\) from a raw pitch having TI toluene insolubles. Plotting the data for pitch A yields Figure 4. It is apparent that both the oxygen and hydrogen treated pitches fall on a single line. The slope of the line indicates an apparent TI content in the raw pitch of 39% (correlation 0.894), somewhat higher than the 22% observed experimentally. The high value of the apparent TI indicates that the sparged samples contain more TI fraction than would be expected if the sparge reaction was a simple volatilisation of toluene soluble species. This is a surprising result, since it would be expected that at least some of the toluene insolubles would themselves be volatile and hence the apparent TI value should be lower than experimental observation. It is apparent from this that some combinatorial chemistry is occurring during the gas sparge process, which is increasing toluene insolubility but which for this sample does not affect carbon yield.

When the same analysis is conducted with pitch B there is again a marked difference between the oxygen and hydrogen data which fall on two separate straight lines, Figure 5. The hydrogen data yields an apparent TI for the raw pitch of 41.5% (correlation 0.987), again somewhat above the experimental result of 28%. This is presumably explicable by the same argument as for pitch A. The oxygen data gives a reduced slope yielding an apparent TI value of 54% (correlation 0.994), much higher
than the experimental value. For the oxygen sparged pitch, the increase in apparent TI of 12.5% correlates closely with the increase in apparent CY of 14%. Unsurprisingly, the additional carbon producing phase introduced by oxygen sparging is also toluene insoluble.

The measured data does not give a reliable indication of the nature of the changes in pitch B brought about by oxygen. It is likely, however, that the reaction will involve either an oxidative molecular growth mechanism, or, alternatively, may simply represent the change in volatility of polyaromatic molecular species brought about by the introduction of oxygen functionality. Comparison of naphthalene, BP 218°C, with 2-naphthol, BP 295°C, can be used to illustrate this point.

4. Conclusions

Studies of the gas sparging properties of two pitches have shown markedly different results.

Pitch A shows some evidence of chemical change, as measured by an increase in apparent TI, with sparging. However, the change is independent of the chemical nature of the sparge gas and presumably is thermally induced. The chemical change does not benefit the carbon yield obtained from the pitch when this is calculated based on the original pitch mass.

Pitch B shows similar properties to pitch A when sparged with a hydrogen containing gas. However, the use of an oxygen containing gas produces an increase in both TI fraction and in carbon yield.
The implication of this work is that hydrogen sparging produces chemical change in both pitches. The nature of the chemical change is probably a molecular growth mechanism which introduces somewhat labile bonds which are unable to survive the pyrolysis reaction.

With oxygen sparging, pitch A shows no change relative to hydrogen sparging. Pitch B shows a marked improvement in carbon yield and Ti indicating that chemical changes are occurring. The oxidative changes in pitch B produce enhanced levels of Ti and are sufficiently stable to increase carbon yield.

The fact that two apparently similar pitches behave so differently is an important finding, which perhaps helps to explain the often contrary results which have been reported in the literature.

5. Acknowledgement

The authors would like to thank the European Coal and Steel Community for financial assistance under research programme 7220-EC767.

6. References


### Table 1. Analytical data for the two pitches studied

<table>
<thead>
<tr>
<th></th>
<th>Pitch A</th>
<th>Pitch B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point/°C</td>
<td>84</td>
<td>111</td>
</tr>
<tr>
<td>Fixed Carbon/%</td>
<td>36.3</td>
<td>37.9</td>
</tr>
<tr>
<td>(to 1000°C at 100°C/hr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentane Insolubles/%</td>
<td>84</td>
<td>90</td>
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<tr>
<td>Toluene Insolubles/%</td>
<td>22</td>
<td>28</td>
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<tr>
<td>Quinoline Insolubles/%</td>
<td>0.1</td>
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### Table 2. Sparge reactor yields

<table>
<thead>
<tr>
<th></th>
<th>Pitch A</th>
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</tr>
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<tr>
<td></td>
<td>Hydrogen</td>
<td>Oxygen</td>
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<tr>
<td>1 Hour</td>
<td>56.7</td>
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</tr>
<tr>
<td>2 Hour</td>
<td>65.7</td>
<td>64.5</td>
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<tr>
<td>4 Hour</td>
<td>50.2</td>
<td>54.5</td>
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</table>
Table 3. Properties of the gas sparged pitches

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Treatment</th>
<th>SP(°C) ± 6°C</th>
<th>CY (%) ± 0.7%</th>
<th>ΔCY/ΔSP</th>
<th>PI (%) ± 1%</th>
<th>TI (%) ± 4%</th>
<th>QI (%) ± 0.3%</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>84</td>
<td>36.3</td>
<td></td>
<td>84</td>
<td>22</td>
<td>0.1</td>
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<tr>
<td>AH1</td>
<td>H₂/1 hour</td>
<td>218</td>
<td>56.5</td>
<td>0.15</td>
<td>97</td>
<td>43</td>
<td>0.5</td>
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<td>AH2</td>
<td>H₂/2 hours</td>
<td>210</td>
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<td>0.12</td>
<td>98</td>
<td>41</td>
<td>0.9</td>
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<tr>
<td>AH4</td>
<td>H₂/4 hours</td>
<td>255</td>
<td>62.4</td>
<td>0.15</td>
<td>97</td>
<td>54</td>
<td>1.0</td>
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<td>AO1</td>
<td>O₂/1 hour</td>
<td>192</td>
<td>50.4</td>
<td>0.13</td>
<td>93</td>
<td>36</td>
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<td>O₂/2 hours</td>
<td>185</td>
<td>48.3</td>
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<td>96</td>
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<td>B</td>
<td>-</td>
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<td>37.9</td>
<td></td>
<td>90</td>
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<td>2.1</td>
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<td>BH1</td>
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<td>178</td>
<td>48.8</td>
<td>0.16</td>
<td>96</td>
<td>42</td>
<td>3.2</td>
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<tr>
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<td>H₂/2 hours</td>
<td>206</td>
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<td>0.17</td>
<td>96</td>
<td>51</td>
<td>5.0</td>
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<tr>
<td>BH4</td>
<td>H₂/4 hours</td>
<td>245</td>
<td>60.4</td>
<td>0.17</td>
<td>100</td>
<td>58</td>
<td>4.8</td>
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<tr>
<td>BO1</td>
<td>O₂/1 hour</td>
<td>189</td>
<td>55.1</td>
<td>0.22</td>
<td>94</td>
<td>46</td>
<td>2.6</td>
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<tr>
<td>BO2</td>
<td>O₂/2 hours</td>
<td>188</td>
<td>56.5</td>
<td>0.24</td>
<td>96</td>
<td>47</td>
<td>3.1</td>
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<tr>
<td>BO4</td>
<td>O₂/4 hours</td>
<td>233</td>
<td>63.9</td>
<td>0.21</td>
<td>98</td>
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<td>±1</td>
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<td>±7</td>
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