DEVELOPMENT OF CARBON FIBRE REINFORCED CARBON COMPOSITES

A PROJECT REPORT FOR PARTIAL FULLFILMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF ENGINEERING IN POLYMER TECHNOLOGY

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CERTIFICATE

This is to certify that the project entitled **" DEVELOPMENT OF CARBIN FIBRE REINFORCED CARBON COMPOSITES "** submitted by **Mr. AJAY RAJPUT**, student of **Master Of Engineering** (Polymer Technology) from Delhi College Of Engineering, Delhi. Work carried by him under joint supervision of Dr. G.L. Verma, Head, Department Of Applied Chemistry, Delhi College Of Engineering, Delhi and Dr. G. Bhatia, Scientist 'F' and Head, Carbon Technology Unit, National Physical Laboratory, New Delhi.

His work has been found excellent for the partial fulfillment of the requirement for the degree of M.E. This report has not been submitted in part or full in any other University for award of any degree or diploma.

Period of project starts from 4th January 2006 to 30th June 2006.

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CONTENTS

1.0 INTRODUCTION

Carbon and graphite manufacture is a world-wide industry which is growing up rapidly because of the increasing interest being taken in this material by scientists and technologists, both. This is because of the fact that this material exhibits a unique combination of physical, chemical, metallurgical, mechanical, electrical, thermal and nuclear properties. Carbon and graphite products, in one form or the other, form indispensable components of almost all major industries, and thus they act as the backbone of the industrialization of a country. In fact, these products form an important part of our day-to-day life. Graphite electrodes for the steel industry, carbon anodes and cathodes for the aluminium industry, carbon lining for the electrolytic cell in the production of caustic soda, calcium carbide etc., carbon brushes for the electric motors and generators, carbon granules for the telephone receiver sets, carbon crucibles for the melting of metals and alloys, carbon seals and bearings for mechanical applications, nose-cones and nozzle inserts for missiles and rockets, leading edges and brake pads for military and advanced civilian aircrafts, and moderator and reflector for nuclear reactors are some of the examples showing the vast applications of carbon and graphite. Recently, there has been an increased interest in this material, than ever before, and as a result, several newer carbon products have come into existence. Carbon fibres, carbon fibre based composites, glassy carbon, high density - isotropic graphite, high thermal conductivity graphite, fullerenes, nanotubes are examples of some such products. These products are further widening the scope of the applications of this fascinating material.

Carbon-carbon composite have important properties such as high specific strength and stiffness up to the highest temperature and excellent dimensional stability due to their very low thermal expansion coefficient. They increasingly qualify as materials for advanced and highly specified applications. The fabrication of such materials can be manipulated to alter the type and the distribution of the carbon fibers which themselves can be modified according to structural need and also to alter the carbon or graphite matrices that binds these fibers. Such manipulations would enable the designer's specific requirements to be met.

In this work, we will be dealing with pitch based carbon materials and an carbon fibre reinforced carbon composites which will be developed with pitch as matrix precursor. The transformation of pitch into a carbon material requires a carbonization process. Coal-tar pitches are complex mixtures of organic compounds, with a highly aromatic character. When heated, pitch softens and becomes liquid. Further heat treatment involves the release of volatiles and reactions of dehydrogenative polymerization and condensation, leading to large planar aromatic molecules (mesogens). The mesogens can be segregated from the isotropic pitch to give rise to a secondary liquid crystal phase known as a mesophase. As the mesophase becomes the continuous phase, the viscosity of the system increases rapidly and eventually the material solidifies into a coke (carbon which can be graphitized). The optical texture of cokes (size, morphology and orientation of the crystalline structures observed under the microscope) and porosity contribute to the properties of the carbon material. The composition of the parent pitch and pyrolysis conditions affect the evolution of mesophase and therefore the optical texture of the coke. One of the industrial specifications of coal-tar pitches when they are for commercial use in the manufacture of electrodes is their quinoline insoluble content (QI). These QI are made up of carbonaceous particles, <1 μm in diameter, which are produced by the thermal cracking of volatile products during the coal coking process. It is generally held that QI restrict the development and coalescence of the mesophase, and hence a QI free pitch or a pitch containing <0.5% QI is preferred as matrix in the development of carbon products like C-C composites and green coke based products.

1.1 REVIEW OF LITERATURE

1.1.1 THE ELEMENT 'CARBON'

Carbon has an atomic weight of 12.011 and an atomic number of 6. The electronic ground state $2s^2$ $2p^2$ is almost unknown because of the energetic advantage of involving all the four outer orbital electrons in bonding between carbon atoms themselves, or with other atoms. Carbon displays catenation (bonding to itself) to a unique degree, which results in structure of chains, rings, and networks. In most chemical compounds, carbon is tetravalent because of the transition of one electron from the 2s orbital to the 2p orbital, resulting in the excited state configuration $1s^2$ $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$. These 's' and 'p' orbitals in the outer shell undergo hybridization to give hybrid orbitals. In diamond, one 's' and three 'p' orbitals hybridise to give four sp^3 hybridised orbitals, resulting in a tetrahedral structure with a bond angle of 109°28'. In graphite, one 's' and two 'p' orbitals hybridise to give three sp^2 hybridised orbitals, resulting in a planar triangular structure with a bond angle of 120°.

1.1.2 STRUCTURE OF DIAMOND

Diamond (Fig.1) has a face-centered-cubic structure with an interatomic distance of 1.54 A°. Each atom is covalently bonded to four other carbon atoms in the form of a regular tetrahedran[1]. The three dimensional isotropic structure accounts for the extreme hardness of diamond. Diamond is stable and chemically inert at moderate temperatures. However, at temperatures above 1500 ℃ in the absence of air, it is transformed into graphite[2]. Diamond can be synthesized from graphite at a pressure of about 85 K bars and a temperature of about 1600 ℃[3].

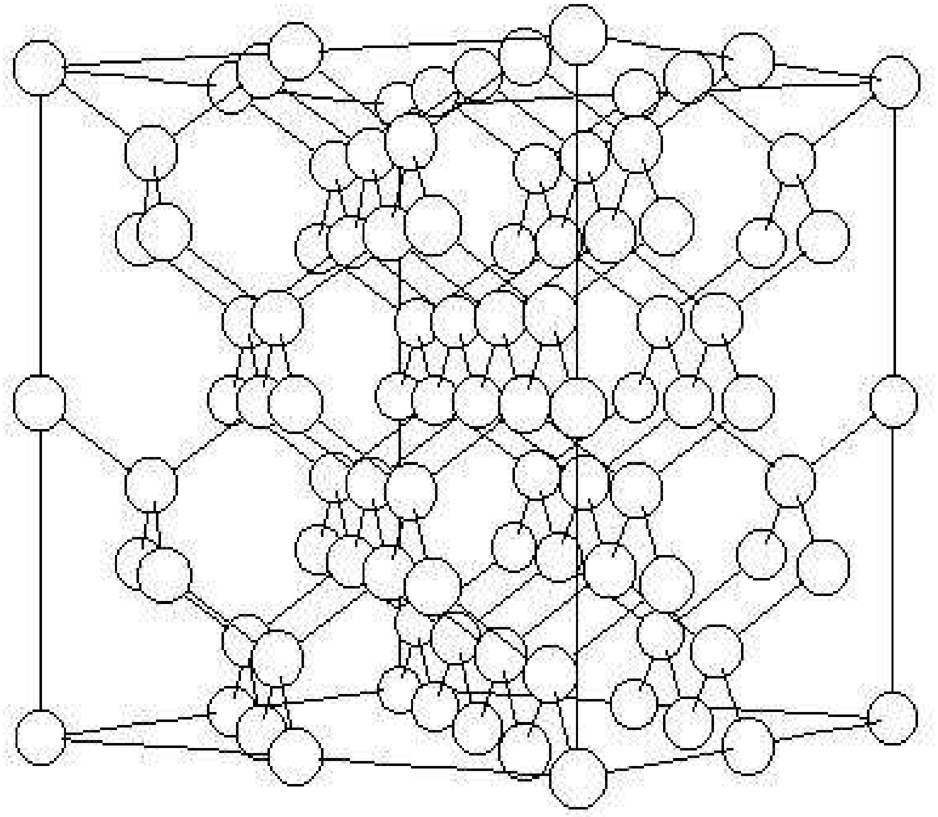
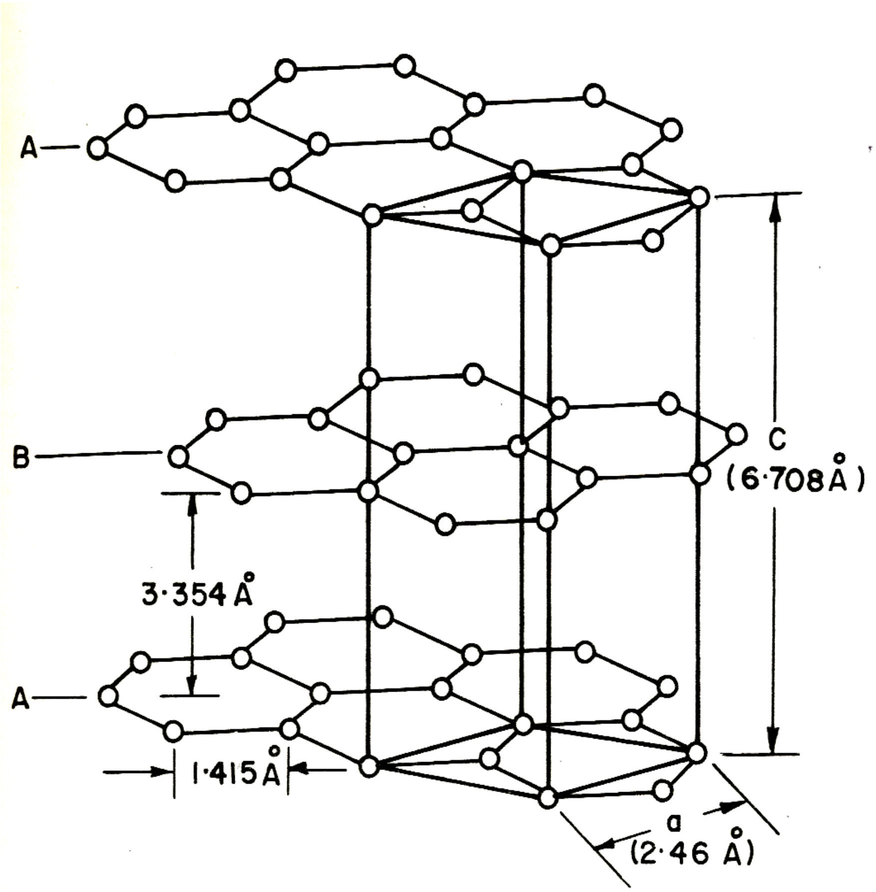


Fig.1: Structure of diamond

1.1.3 STRUCTURE OF IDEAL GRAPHTIE

The structure of ideal graphite was first proposed by Hull [4] in 1917 and later confirmed by Bernal [5] in 1924. It consists of parallel plane layers of carbon atoms covalently bonded in a regular open-centered hexagonal array. The layers are bonded together by weak van der Wall's forces at a separation of 3.354 A°in a (AB AB AB .. .. ..) stacking sequence, as shown in Fig.2, in such a way that atoms in alternate planes align with each other. Within each layer, C-C distance is 1.415 Å. The three sp^2 hybridised orbitals of each carbon atom form bonds with adjacent carbon atoms and the fourth electron in the 'p' orbital gives conjugated bonding. This results in delocalization of the **p** -electrons throughout the layer structure.

A less frequently occurring structure is rhombohedral with ABC ABC … … stacking arrangement in which the atoms of every fourth layer align with each other[6,7]. This rhombohedral form, which occurs only in conjunction with hexagonal form, is less stable, and converts to the hexagonal form irreversibly at 2100 °C[8]. The bond energy between planes is 17 KJ mole^{-1} and within planes is 477 KJ mole^{-1}. Graphite sublimes at a temperature of 3640 ± 25 °K at atmospheric pressure. However, it may be made to melt under a pressure of 125 ± 15 atmosphere at a temperature of 4020 ± 50 °K[9,13]. This temperature of about 4000 °K has been moved to about 5000 °K by way of more accurate measurements[14].



<u>Fig. 2:</u> Structure of ideal graphite

1.1.4 STRUCTURE OF FULLERENES

Fullerenes represent the third allotropic crystalline form of the element Carbon, referring to a new class of discrete molecules. C_{60} molecule was first reported by Kroto et al. in 1985 in the mass spectrum of laser-ablated graphite[15]. Five years later, in 1990, W. Kratschmer et al. reported evidences for the presence of C_{60} in a sample of carbon dust prepared from vaporized graphite[16] and they were able to isolate macroscopic quantities of C_{60} and C_{70} [17] molecules. Fullerenes can be considered as networks of pentagons and hexagons. Such molecules invariably have twelve pentagons in order to close into a spheroid although the number of hexagons varies widely. Examples of Fullerenes are C_{60}, C_{70} and C_{240} molecules. The C_{60} molecule contains 20 hexagons. It is the roundest of all fullerene molecules and its structure is shown in Fig 3 Its stability can be explained by the molecular structure having perfect symmetry of a soccer ball.

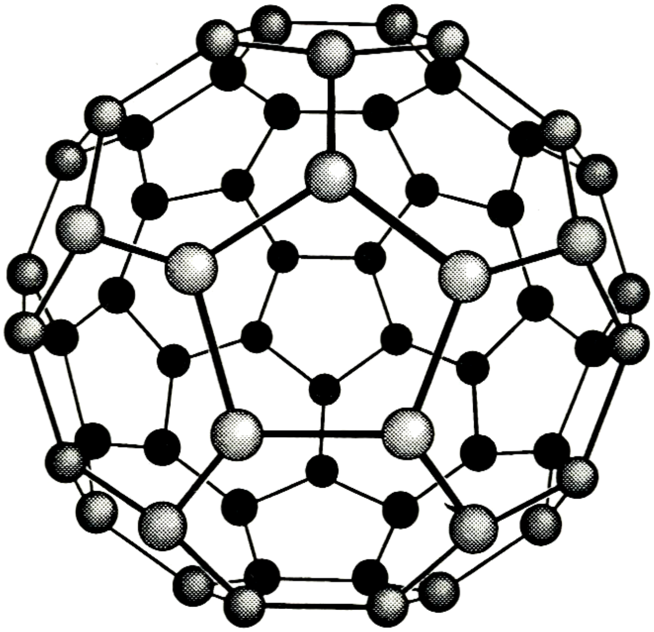


Fig. 3 Structure of C_{60} fullerene molecule

1.1.5 STRUCTURE OF CARBON NANOTUBES

In 1991, Iijima[18] discovered a cylindrical form of the ‘bucky ball’, known as a carbon nanotube. (Fig.4). Nanotubes fall into two broad classes – multiwall and single wall. Carbon nanotubes are unique tubular structures of nanometer diameter and large length-to-diameter (aspect) ratio. The nanotubes may consist of one up to tens and hundreds of concentric shells of carbon atoms with adjacent shells separation of ~ 0.34 nm. The carbon network of the shells is closely related to the honeycomb arrangement of the carbon atoms in the graphite sheets. The amazing mechanical and electronic properties of the nanotubes stem in their quasi-one-dimensional (1D) structure and the graphite-like arrangement of the carbon atoms in the shells. Thus, the nanotubes have high Young’s modulus and tensile strength, which makes them preferable for composite materials with improved mechanical properties. The nanotubes can be metallic or semiconducting depending on their structural parameters.

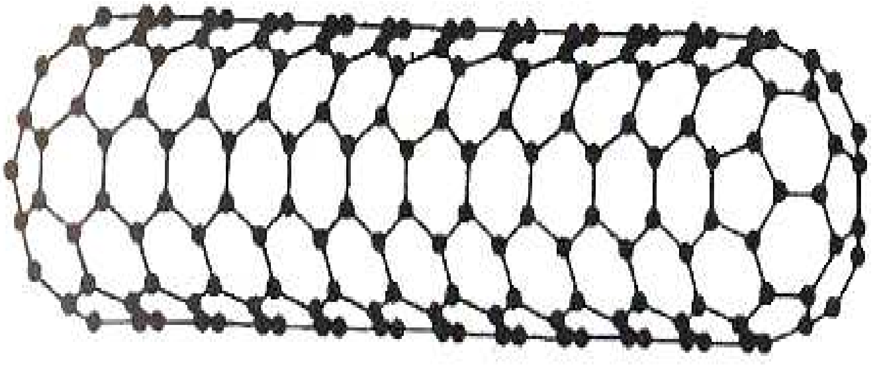


Fig. 4: Structure of carbon nanotubes

1.2 CARBON FIBRES

1.2.1 HISTORY OF CARBON FIBRES

Carbon fibres are fibrous carbon materials with carbon content more than 90%. They are transformed from organic matter by 1000-1500°C heat treatment, which are the substance with imperfect graphite crystalline structure arranged along the fibre axis. There are two ways to produce carbon fibres : one is from organic precursor fibres, the other is from gas growth. The first commercially produced carbon filament was made from a cellulosic precursor for its application as incandescent lamp filaments in 1879. Cotton threads and later bamboo fibres were formed into filaments of desired size and shape and then baked to a substantially all carbon replica of the original filament. Systematic work regarding the carbonization of Rayon and PAN yarns and fabrics was initially investigated by Union Carbide Corp. during the world war II as a possible substitute to material for control grids in the vacuum tube power amplifiers. Two processes for manufacturing high strength and high modulus carbon fibres from organic fibres (Rayon and PAN) were invented almost simultaneously in 1959 and 1961. four years latter in 1963 a high modulus carbon fibre (structure shown in Fig.5) made from pitch was invented[21].

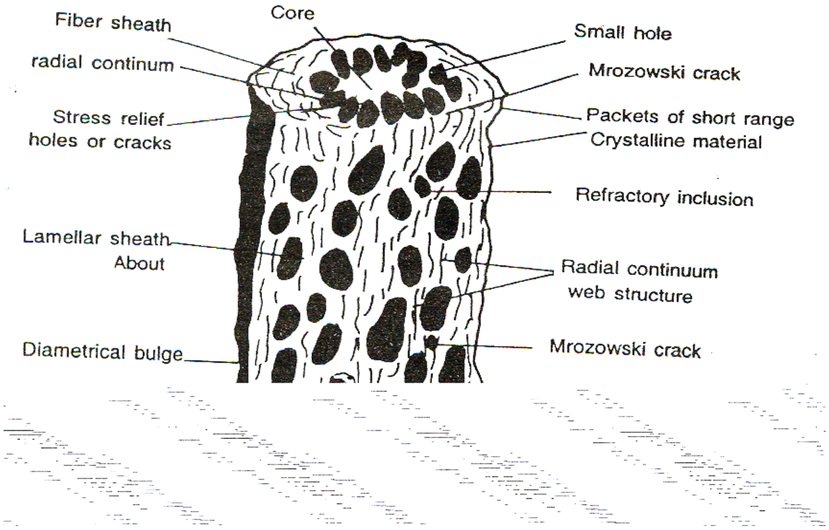


Fig. 5: Structural model for high modulus carbon fibres[20]

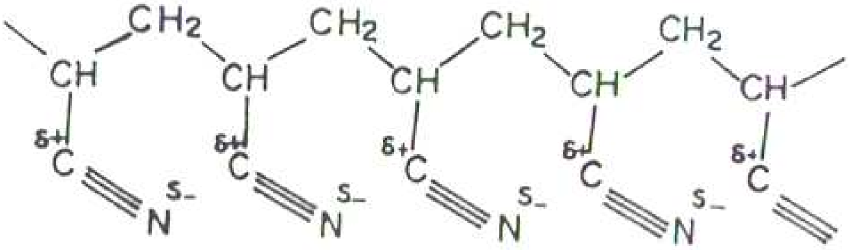
Since the final carbon fibre contains almost 100 % carbon, any fibrous material with carbon back-bone could be used as precursor which would yield carbonaceous residue upon heat treatment. Many naturally occurring materials such as cotton, jute, linen, ramie, sisal and man made polymers like polyester, polyamides, polyvinyl chloride, polyvinyl alcohol, phenolic resins, syndiotactic 1,2 polybutadiene, polyethylene, etc. have been tried as possible precursor for carbon fibre manufacture.

Ultimately, three precursors namely viscous rayon (regenerated cellulose), pitch and polyacrylonitrile have received major attention for making carbon fibres with attractive mechanical properties[21].

1.2.2 POLY ACRYLONITRILE-BASED CARBON FIBERS

Polyacrylonitrile (PAN) is the only precursor which has found maximum attention, as of today, for developing high performance carbon fibers. Almost seventy to eighty percent of commercially available carbon fibers are basically derived from PAN polymer [(CH2CHCN)n]. It scores over other two predominant precursors namely viscose rayon and pitch, mainly because of the following reasons[22].

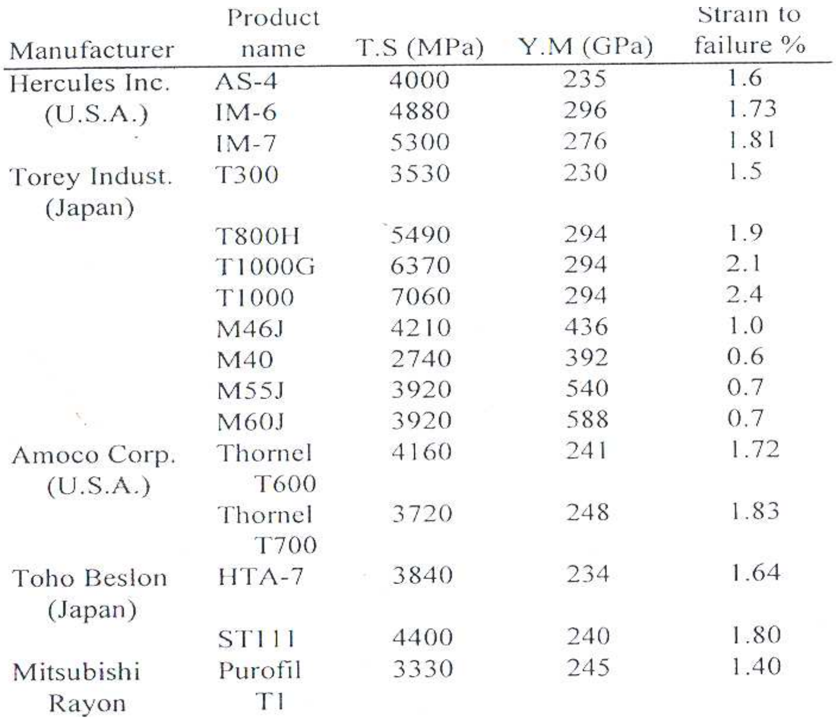
I. Its structure, shown in Figure 6, permits faster rate of pyrolysis without much disturbance to its basic structure and to the preferred orientation of the molecular chains along the fiber axis present in the original fiber.
2. It decomposes before melting. .
3. Higher degree of preferred orientation of the molecular chains is possible during spinning wherein PAN can be stretched to as high as 800%. Further improvement in the orientation is also possible during thermal stabilization when it becomes plastic at around 180℃ and through various post spinning modifications.
4. It results in high carbon yield (50-55%) when pyrolized to 100O℃ and above.



<u>Fig. 6:</u> Structure of PAN

1.2.3 PAN to Carbon Fibers

First step in the processing is polymerization. Next is *of* spinning to obtain the polyacrylonitrile fibers. For developing carbon fibers from *PAN* fibers, first step is thermal stabilization. It is achieved by heating PAN fibers in the oxidizing atmosphere, usually air, at 200-300℃ under application of load. This stabilized fiber is then treated in inert atmosphere to 1500℃ to get the high strength carbon fibers known as "type II" carbon fibers. If the heat treatment is carried further to beyond 2500℃, the carbon fibers obtained are *of* high modulus and known as type I carbon fibers. Mechanical properties of some commercially available PAN fibres are shown in Table 1.



Manufacturer	Product name	T.S (MPa)	Y.M (GPa)	Strain to failure %
Hercules Inc. (U.S.A.)	AS-4	4000	235	1.6
	IM-6	4880	296	1.73
	IM-7	5300	276	1.81
Torey Indust. (Japan)	T300	3530	230	1.5
	T800H	5490	294	1.9
	T1000G	6370	294	2.1
	T1000	7060	294	2.4
	M46J	4210	436	1.0
	M40	2740	392	0.6
	M55J	3920	540	0.7
	M60J	3920	588	0.7
Amoco Corp. (U.S.A.)	Thornel T600	4160	241	1.72
	Thornel T700	3720	248	1.83
Toho Beslon (Japan)	HTA-7	3840	234	1.64
	ST111	4400	240	1.80
Mitsubishi Rayon	Purofil T1	3330	245	1.40

Table 1: Mechanical properties of some commercially available PAN

1.2.4 RAYON BASED CARBON FIBRES

Another important raw material for producing carbon fibers which degrades without melting is cellulose. Natural cellulose fibers such as those of cotton and ramie are not preferred for the production of carbon fibers because these are discontinuous in nature and exhibit a low degree of orientation in addition to having impurity materials such as lignin. Accordingly, they are considered inferior to synthetic cellulose fibers. The most commonly employed cellulosic fibers for producing carbon fibers are textile grade rayon, regenerated cellulose, and cuprammonium rayon, although polynosic rayon and viscose rayon fibers have also been used as precursors far making carbon fibers.

These high modulus rayon based fibers were used extensively in the evelopment of polymer matrix composites for space structj.lres. In recent years, the less costly high modulus PAN based carbon fibers have substituted for the rayon based fibers. However, because of the properties 'of low density, high purity (content of alkaline and alkaline-earth metal is less than 50-100 ppm), low heat conductivity and high strain, rayon-based carbon fibers are now still used in aerospace industry, especially used as missile's thermal protection material. In addition, they are also used in medical and other industries and there is still production in the United States and Russia[23].

1.2.5 Processing

Following are the three main stages involved in the development of carbon fibers from rayon.

a. Low temperature decomposition (< 400℃).
b. Carbonization « I 500℃).
c. Graphitization (> 2500℃).

The yield of carbon fibers obtained by pyrolysis of rayon is usually in the range of 10 and 30% and depends upon the nature of the precursor fibers and the processing parameters. The molecular weight of the cellulosic precursor plays a vital role as it determines the number of end groups available for initiation of the degradation process. A slow rate of heating results in a higher yield but it is less economical, and for that reason, pyrolysis is carried out in a suitable reactive atmosphere . This changes the course of the decomposition process so that it occurs at a lower temperature but at a much faster rate and results in a greater yield of the carbon fiber . Since cellulosic materials suffer disruption of each ring to ring linkage and extensive weight loss, the graphitization is usually carried out under stress so that the atoms can be juxtaposed to fit into the graphite crystal.

Table 2: Mechanical Properties of Some Commercially Available Rayon Based Carbon Fibers

Manufacturer	Product name	T.S (MPa)	Y.M (OPa)
Amoco Corp.	Thomol 50	2070	345
	Thomo!75	2520	517
	Thornol 40	1720	276
Hitco (U.S.A.)	HMO. 50	.70	345
	HMO 40	1720	276
	HMO 25	1030	172

1.2.6 PITCH BASED CARMON FIBERS

Pitch-based carbon fibers provide properties not readily obtainable with PAN-based fibers. Whereas the PAN-based fiber has excellent strength at a modulus of 200 GPa, strength decreases as the modulus is increased, and the upper limit of modulus is about 650 GPa. Pitch-based fibers are capable of modulus levels up to the theoretical modulus of graphite, 1000 GPa, and have much better thermal and electrical conductivity properties than PAN-based fibers. Pitch and PAN-based fibers should be considered complementary, each filling a different set of commercial needs.

The raw materials for pitch are abundant and cheap. They are by-products of petroleum and coal-chemical industry (such as petroleum refined residue, coal tar, and pitch, the residue of solvent refined coal and petroleum) and some pure aromatic hydrocarbon (such as naphthalene, anthracene). Isotropic and anisotropic pitch with proper softening point and good spinnability can be purified by the methods of thermal modification, solvent modification , hydrogenation and catalytic modification etc. Then, followed melt spinning, stabilization, carbonization, graphitization, surface treatment and sizing, general performance carbon fiber (GPCF) and high performance carbon fiber (HPCF) can be manufactured, respectively. A manufacturing process of carbon fibers from pitch is presented in Figure 9, and the properties of GPCF and HPCF are shown in Table 3[24].

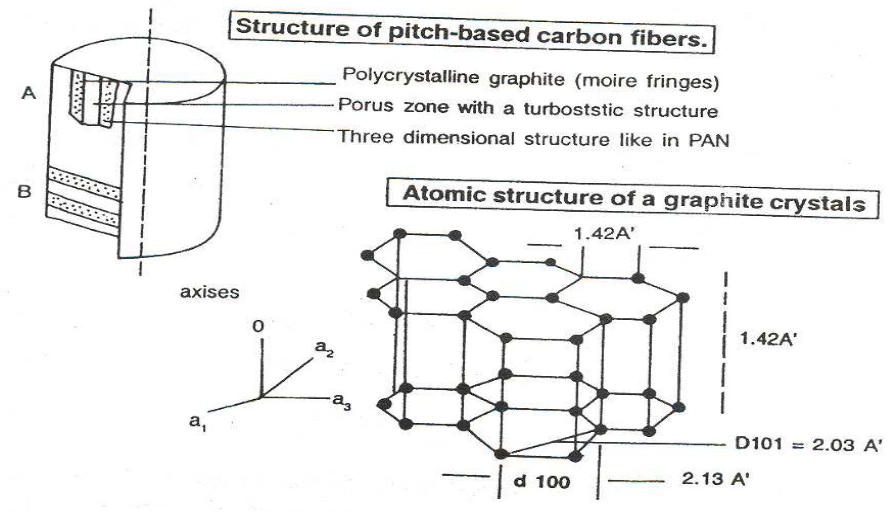


Fig. 7: **Structure of pitch based carbon fibres[26]**

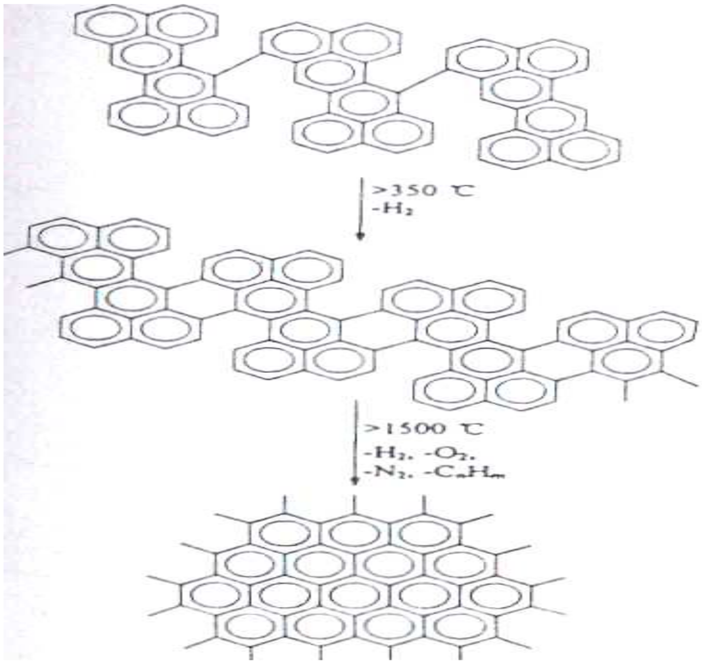


Figure 8: **Schematic change of chemical structure of pitch fiber during thermal treatment process**

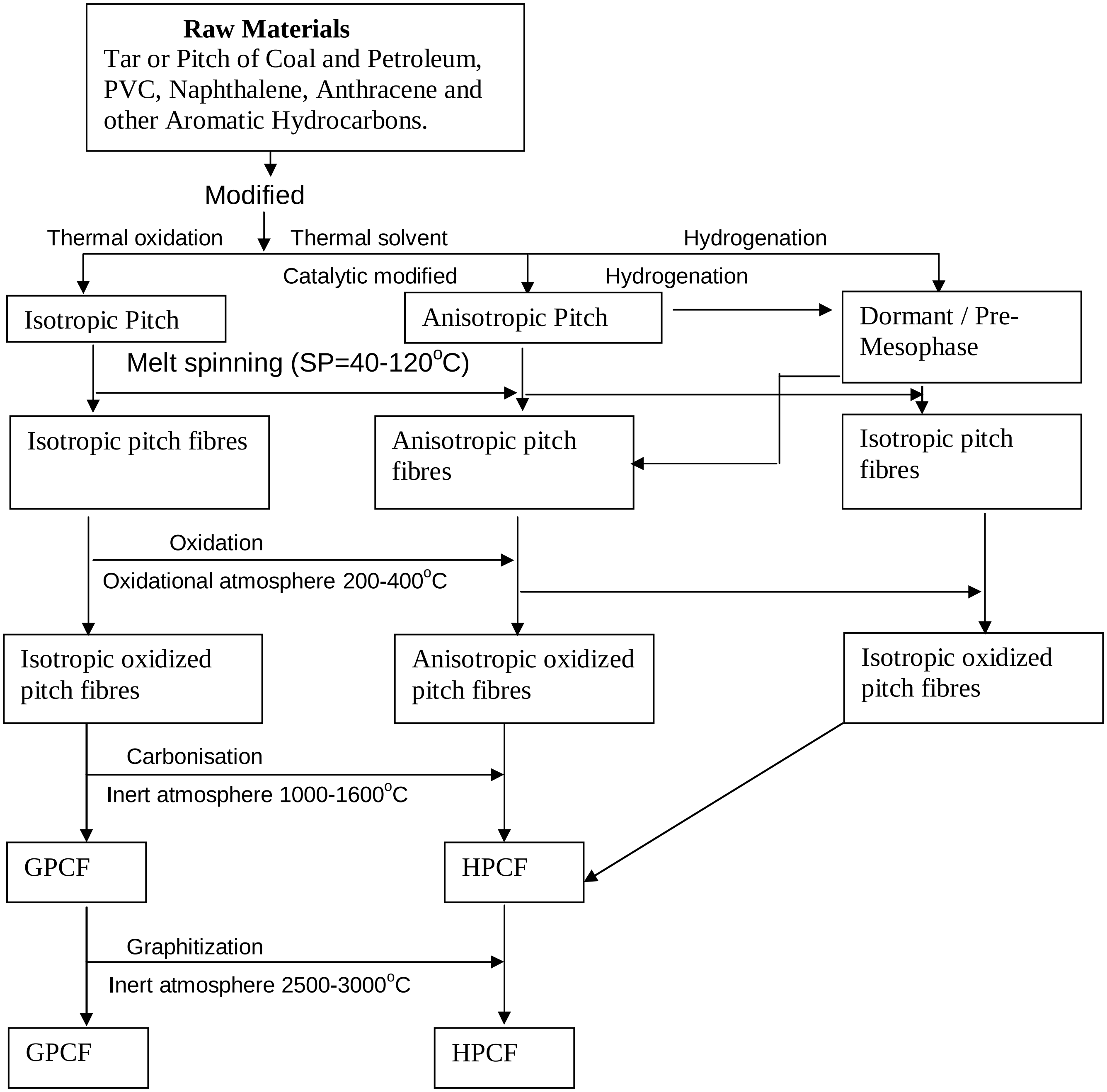


Fig. 9: **Schematic process of manufacture for pitch-based carbon fibres**

Table 3: Mechanical Properties of Some Commercially Available Pitch Based Carbon Fibers

Manufacturer	Product name	T.S(MPa)	Y.M(GPa)	Strain to failure %
Amoco Corp	Thornol P25	*1400*	140	1.0
	Thornol P555	*2100*	380	0.5
	Thornol P755	2000	500	0.44
	Thornol P100	2200	690	0.3
	Thorno! P120	2200	820	0.2
Osaka gas	Danacarb F 140	1800	]40	1.3
	Danacarb F60	3000	600	0.5
Kureka	Kureca KCFIOO	*900*	38	2.4
(Japan)	Kureca KC2IOO	*850*	42	2.1

1.1.2.7 VAPOR GROWN CARBON FIBERS

Vapor grown carbon fibers (VGCFs) are prepared by the decomposition of gaseous hydrocarbons at temperatures between 300 and 2500℃ in presence of an ultra-fine metallic catalyst (e.g. Fe, Ni, and Co). VGCFs are characterized by the high preferred orientation *of* graphitic basal planes parallel to the fiber axis with annual ring texture in the cross-section, which give high mechanical performance, excellent electrical conductivity and high graphitizability to the fiber. Two methods *of* forming VGCFs have been developed: Seeding catalysts on a substrate and fluidizing catalysts in a space. VGCFs may be grown on several types *of* substrates (e.g. carbon, silicon, quartz) and from many hydrocarbons (e.g., acetylene, benzene, natural gas, etc.), but in all cases, growth is favored in a hydrogen atmosphere. The apparatus used by Endo for growing vapor carbon fibers on substrate is shown in Figure 10. Filament diameter may range from about 100 nm' to several hundred micrometers. The process leads to the formation *of* fibers having various cross-section, namely circular, helical, twisted, or pleated fibers[25].

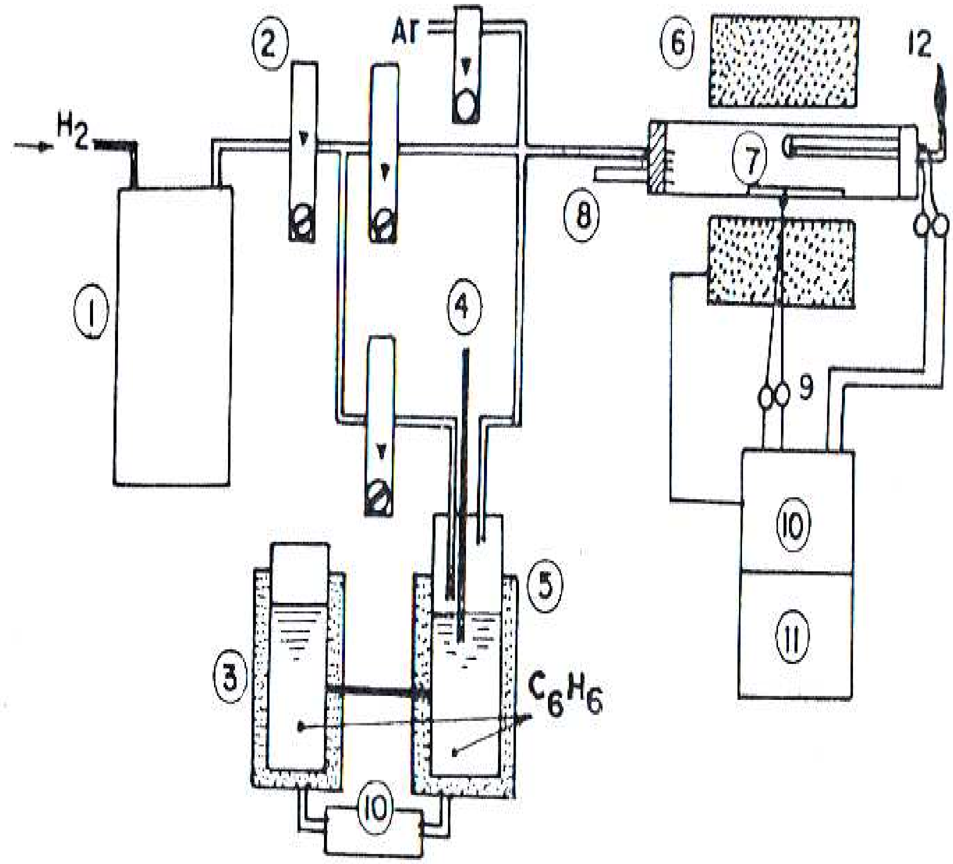


Fig. 10: Schematic diagram of apparatus for preparing carbon fibres by thermal decomposition of hydrocarbons (1) hydrogen purification unit, (2) flow meter, (3)benzene reservoir, (4) thermometer, (5) thermostatic bath, (6) electrical furnace, (7) substrate, (8) peephole, (9) thermocouples, (10) temperature controller, (11) temperature recorder, and (12) gas exhaust.

2.0 PITCH

2.1 Introduction

According to the definitions given by the International Committee for Characterization and Terminology of Carbon (ICCTC) coal-tar pitch is a residue produced by distillation or heat-treatment of coal-tar (coke oven tar) while petroleum pitch is a residue from heat-treatment and distillation of petroleum fractions. Both coal-tar pitch and petroleum pitch are complex mixtures of numerous organic compounds predominantly polycyclic aromatic hydrocarbons (PAH). In addition to PAHs coal-tar pitch also contains hetero-aromatic compounds while petroleum pitch is relatively rich in alkyl substituted PAHs.

Due to their polycyclic aromatic nature pitches form, upon thermal treatment, isotropic or anisotropic cokes in high yield. Almost all applications of pitches rest on this characteristic chemical property. Thus, pitches are important raw materials for the manufacture of engineering carbon and graphite materials such as anodes for aluminium smelting or graphite electrodes for the electric-arc production of steel.

In recent years pitches have increasingly been used in the fabrication of new high performance carbon materials, *e.g.,* carbon-carbon composites or carbon fibres[27].

2.2 Coal- Tar Pitch Production and Formulation

The raw material for the production of coal-tar pitch, *i.e.,* crude coal-tar, is obtained as a by-product of metallurgical coke production. Large-scale carbonization of hard coal to produce blast-furnace coke is performed at temperatures between 1000 and 1200 ℃ and residence times of 14 to 20 hours. Besides coke as the main product (75 wt. %, relative to feed coal) coke oven gas, water, benzene, ammonia and crude coal-tar are obtained. The tar yield amounts to approximately 3.5 wt. %, relative to feed coal. The 750 to 850 ℃ hot gaseous products which are released during carbonization are taken to the gas-collection main where the crude gas is quenched to around 80-100 ℃ by ammonia liquor, removing 60-70 % of the crude tar. The remaining 30-40 % of the tar is obtained on cooling the crude gas in the gas pre-cooler to around 25 ℃.

The crude tar is not completely inert during distillation, and some tar constituents such as acenaphthylene, anthracene or indene are partially converted into the corresponding hydroaromatic compounds as shown in Figure. Hydrogenation very probably occurs by hydrogen transfer where the hydrogen stems from polycondensation reactions of highly reactive large aromatic molecules present in the pitch[28].

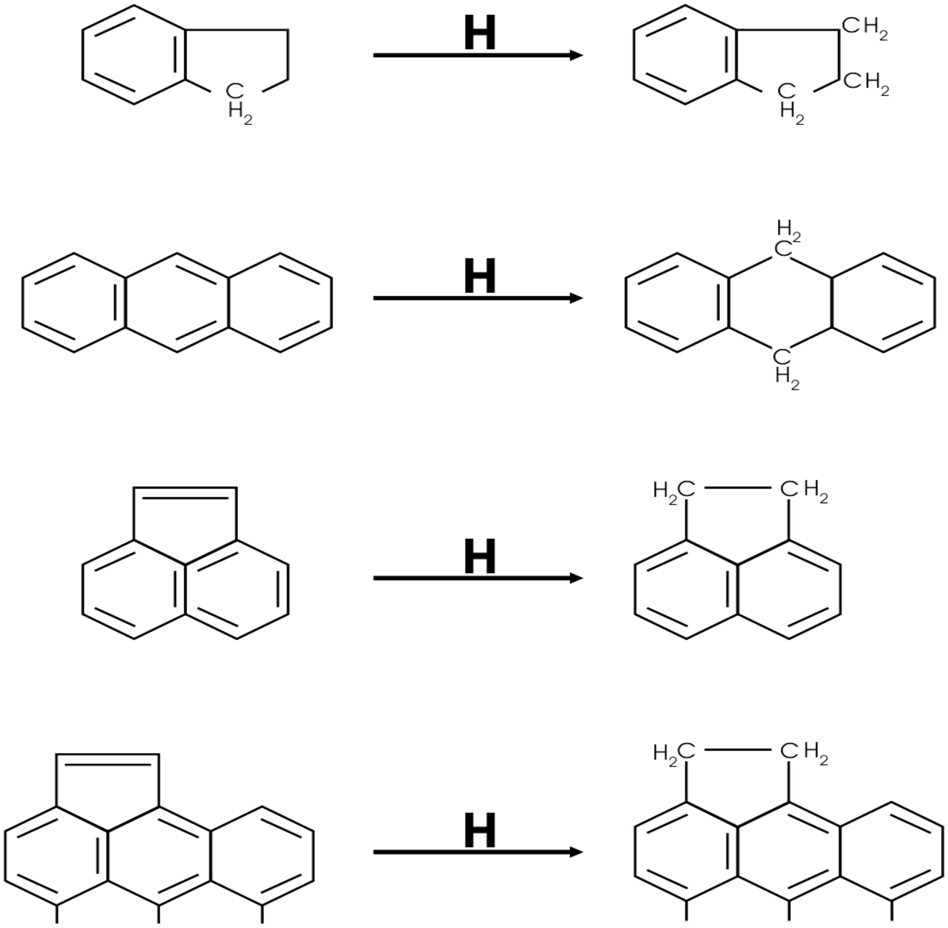


Fig. 11: Thermally induced hydrogenation reactions occurring during tar distillation

The pitch is removed from the tar distillation plant in liquid form and transported in that form (in closed vessels at elevated temperature) or after solidification by cooling with water . Several processes have been developed for this purpose. In one of these the liquid pitch is pressed through heated nozzles into flowing water. The flowing water acts as both cooling and transportation medium. The pitch rods pass through water cooled tubes (20-25 m in length). At their ends the separate pitch rods are sufficiently cooled down so that they can be taken up from a slowly running transportation band, which is located in a cooling water basin. The solid pitch rods are then led through a drying unit with warm blowing air as the drying medium and subsequently cooled with air at ambient temperature. On loading, the pitch rods break into short rod, like pieces, which can be easily handled *e.g.,* pneumatically.

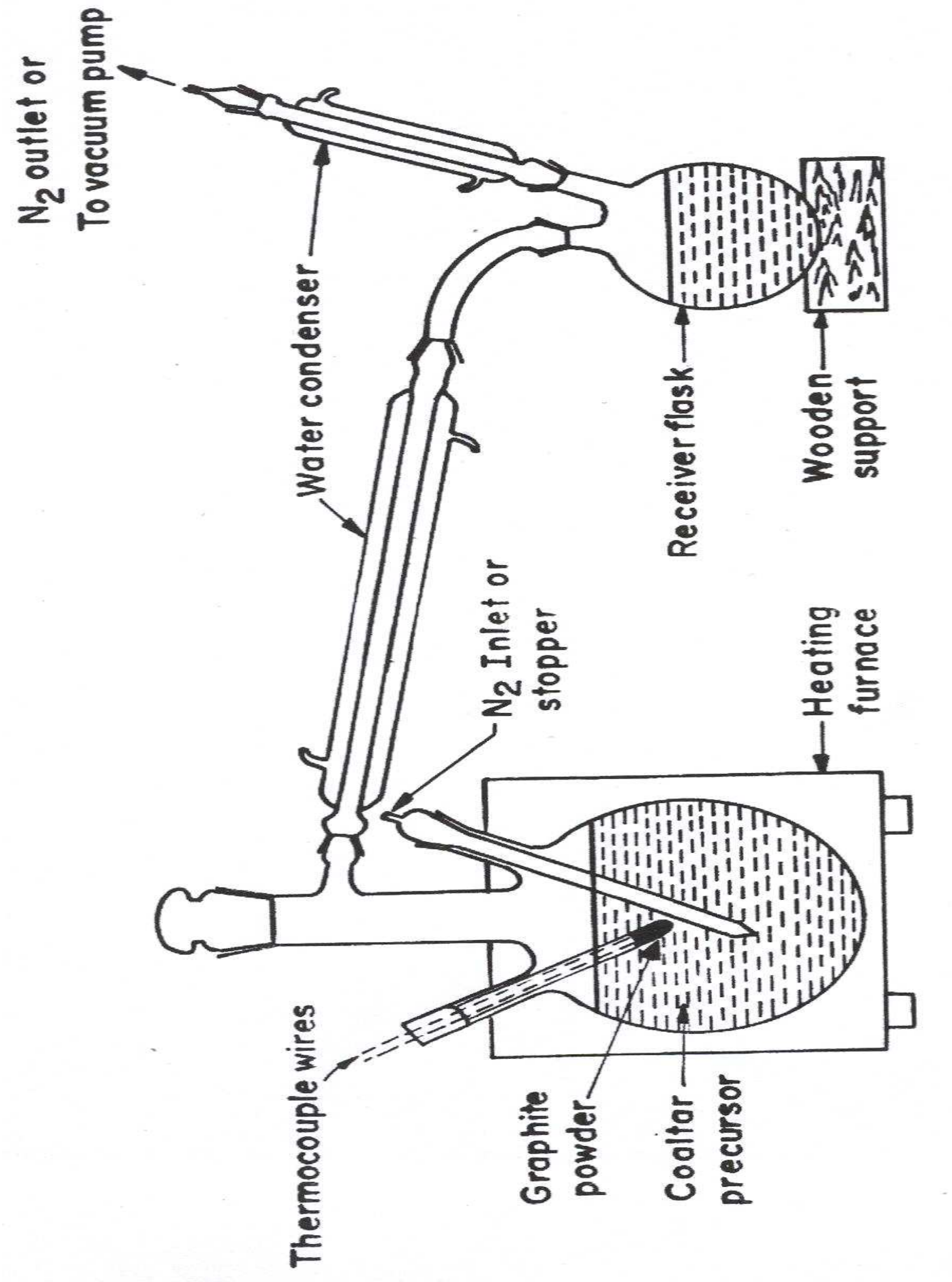


Fig. 12: Schematic of pitch distillation assembly

2.3 Chemical Composition

Coal-tar pitch has a wide molecular weight distribution covering a molecular mass range from approximately 200 to more than 3000 amu. The largest well-defined aromatic compounds that as yet have been detected in coal-tar pitch are a dimer of coronene (molecular mass 596 amu) and dibenzo-coronene (Figure 13). Approximately 97 % of the carbon occurring in coal-tar pitch is present in the form of aromatic compounds, viz. PAHs, structurally related heterocyclic systems and some simple derivatives. Coal-tar pitch consists of an extremely large number of different constituents which, however, belong to relatively few classes of compounds[29].

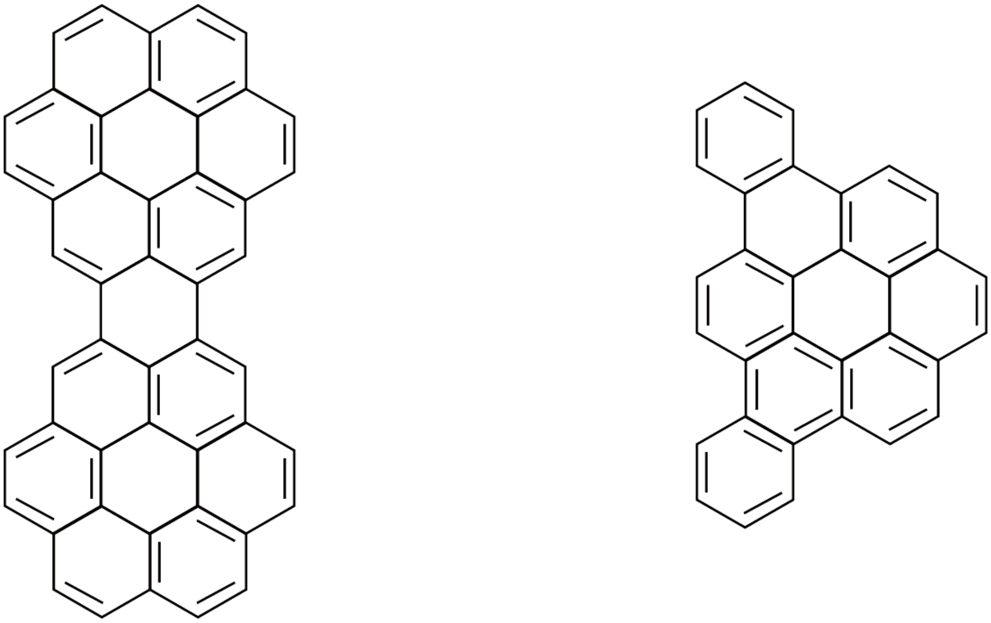


Fig. 13: The largest well-defined compounds that, as yet, have been detected in coal tar pitch

A compilation of the types of compounds present in coal-tar pitch is given below
. Polycyclic aromatic hydrocarbns (P AH).
. Alkylated P AH.
. PAH with cylopenteno moieties ("acenaphthylenes").
. Partially hydrogented P AH.

. Oligo-aryls, Oligo-aryl methanes. . Hetero-substituted PAH: NH2' OH.

. Carbonyl derivatives of PAH.

. Polycyclic hetero-aromatic compounds (benzologs of pyrrol, furan, thiophene, pyridine).

2.4 Physical Properties

Isotropic coal-tar pitch falls into the category of glass-forming materials, *i.e.,* it does not have a defined melting point but on heating 'passes through a glass transition region before forming a viscous liquid. At the glass transition temperature relaxation processes, *i.e.,* molecular translations and rotations become important in realistic time scales. This determines the temperature range over which those properties that depend on these relaxation processes change rapidly. The glass transition temperature can be regarded as the key factor that determines almost all of the physical properties of a pitch (for a detailed discussion of the glassy solid structure and the rheology of pitch).

It is common practice to characterize the rheology of a pitch, not by measurement of the glass transition temperature, but by determination of so-called softening points, which are essentially isoviscous temperatures. The primary QI content of a pitch may have a significant influence on the rheological properties of the pitch. It determines to some degree the wetting behaviour against coke grains, which is of importance in connection with the use of pitch as a binder in carbon anode and graphite electrode production. Most of the rheological properties of a coal-tar pitch depend strongly on the molecular weight distribution of the pitch. For example, it has been shown that the flow behavior of molten pitch on a granular coke bed is related to glass transition characteristics which, on the other hand, depend on the average molecular weight and the polydispersity index of the pitch. Coal-tar pitch as obtained from coal-tar refining is not a single phase system but contains dispersed solid matter. This is partly inorganic (ash) but predominantly organic in nature. Most of the particulate organic matter arises from the gas phase pyrolysis of vapour during coal coking. Its amount in the crude tar and hence in the pitch depends, inter alia*,* on the coking conditions particularly on the extent to which air (oxygen) is present during coking and ranges between a few per cent to more than 10 %. The particulate organic matter present in pitch is often described as being "carbon black-like"[30].

2.5 Petroleum Pitch

Examples of feedstocks that can be used to produce a petroleum pitch include by-product aromatic extracts from lube-oil processes, asphaltic residues from vacuum stills and hard asphalt from solvent deasphalting units, but the currently most important feedstocks are decant oil from fluid catalytic cracking units and the tar-like bottoms (pyrolysis tar) from steamcracking of naphtha and gas oils for the manufacture of ethylene. Pitch can be produced from these feedstocks by thermal treatment, vacuum or steam stripping, oxidation, distillation or a combination of these processes[31].

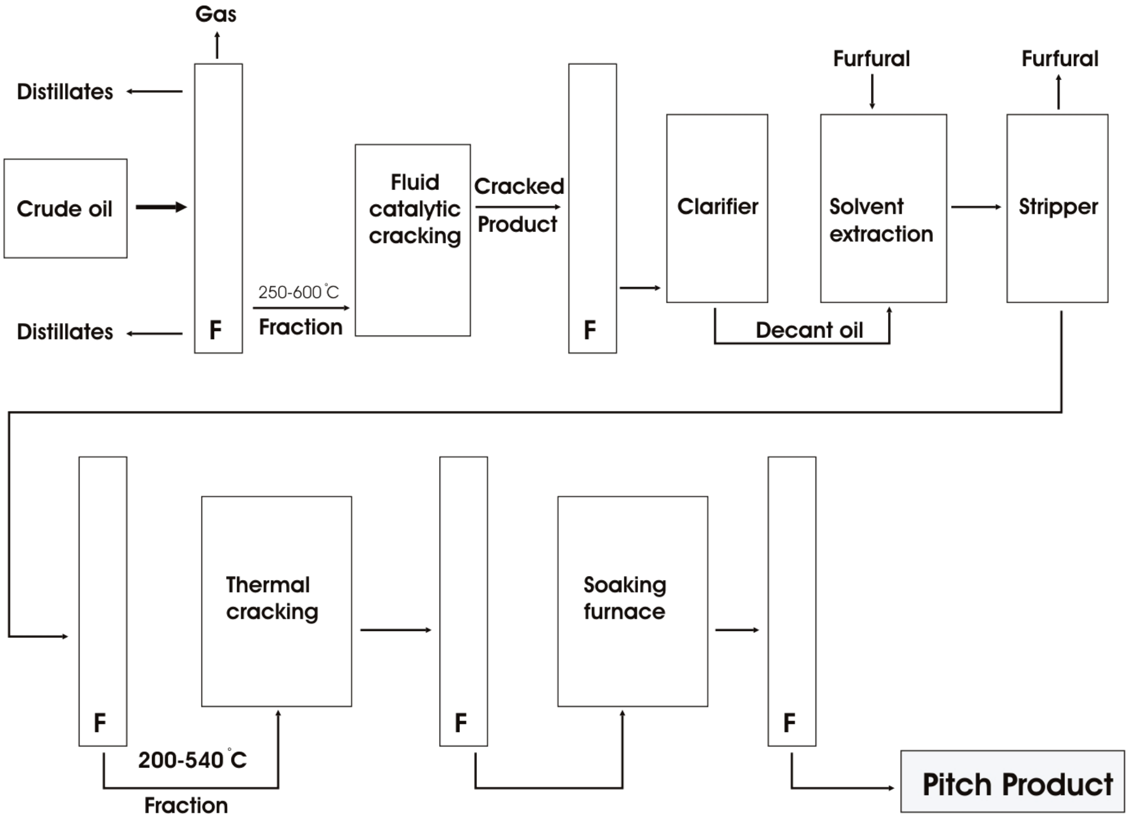


Fig. 14: Schematic representation of a petroleum pitch production

2.6 Physical Properties

The rheological properties of petroleum pitches vary with the feedstocks and processes that were used for their production. For example, if petroleum pitches with identical softening points are compared, the (Brookfield) viscosity is higher for pitches obtained by an oxidation process than for those obtained by thermal cracking. This applies to the entire temperature range studied. The difference is particularly distinct for high-melting petroleum pitches. Also the cold flow (penetration) is higher for oxidized than for thermally cracked pitches. The rheological characteristics of coal-tar pitch are closer to that of thermally cracked petroleum pitches than to those obtained by oxidation[32].

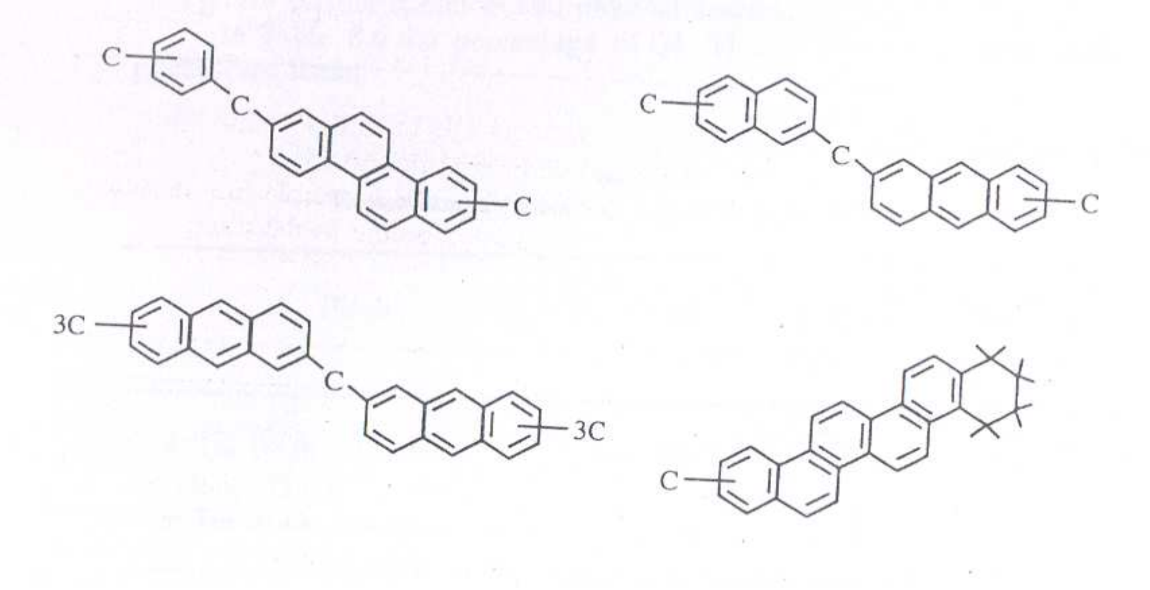


Fig. 15: Typical structures identified in petroleum pitches

2.7 MESOPHASE FORMATION IN PITCHES

The development of mesophase spherules during carbonisation of coal tar and petroleum pitches as well as in various model organic compounds was first reported by Brooks and Taylor[33,34]. Since then numerous contributions have appeared on this subject, which have been very well reviewed by several authors[35-38]. As already mentioned, pitches are complex mixtures of a large number of predominantly aromatic hydrocarbons, their alkyl and hydroxyl derivatives and the corresponding heterocyclic compounds containing oxygen, nitrogen or sulphur. Since the average molecular weight of the various compounds in the pitches is generally 400–600, there is no or little interaction between the molecules, and as a result, these pitches are isotropic in nature[39]. However, when such pitches are heated in an inert atmosphere at 350–450 ℃, dehydrogenative condensation of the molecules takes place resulting in the formation of large planar condensed molecules, which aggregate together to form small liquid crystalline spherules, because of significant Vander Waal's and high surface tension. Within a mesophase spherule, the constituent lamellar molecules lie parallel to the equatorial plane, as indicated by the electron diffraction studies . Optical microscopy indicates that the layers become orientated towards the poles of the spherules and approach the surface of the spherules at right angles, as shown in Fig. 16.

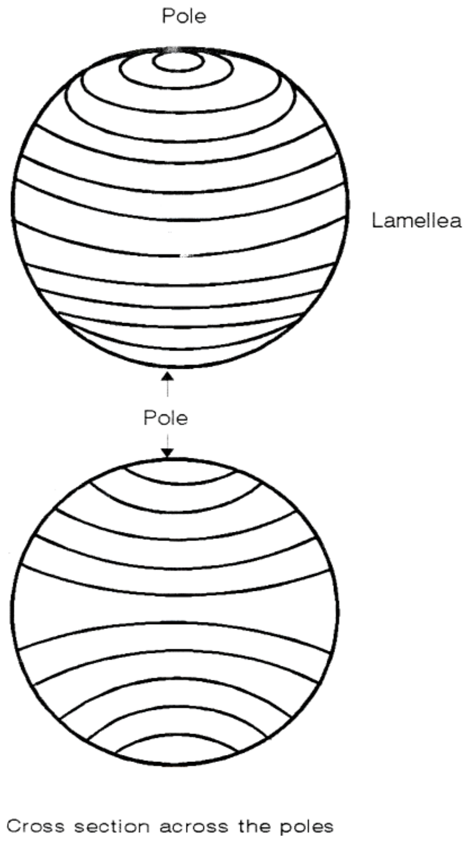


Fig. 16: Structure of a mesophase spherules

On continuation of heating, these spherules grow in size and after about 50% volume concentration , start coalescing to form bigger spherules or masses. This process of growth and coalescence continues with the continuation of heating, resulting eventually in the formation of domains or mosaics of graphite-like parallel layers of planar condensed molecules, which constitute the mesophase.

Bhatia et al. reported on the formation of these mesophase spherules in different fractions of a coal tar pitch and their mixtures . The condition for a good mesophase formation depends to a large extent on the viscosity of the system. It has been observed from the viscosity behaviour of a coal tar pitch, its fractions such as toluene insolubles and their defined mixtures, as well as a petroleum pitch that the toluene insoluble fraction of a coal tar pitch does not reach the necessary minimum viscosity during the heat treatment, as reached by other systems such as pitch itself or the toluene soluble fraction.

It has been known for some time that the solid contents of the precursor pitch should be low if the coke produced is to be highly graphitisable . This is because the solid impurities such as quinoline insolubles (QI) reside over the surface of mesophase spherules and thus hinder their coalescence and subsequent growth. Thus, the size of the mesophase spherules is much lower in a pitch containing quinoline insoluble particles than in its quinoline soluble fraction. In other words, the structure of the final coke is predetermined already in the state of growth and coalescence of mesophase spherules.

3.0 COKES

Coke is a highly carbonaceous product of pyrolysis of organic materials, at least parts of which have passed through a liquid-crystalline state during the carbonisation process. Most coke materials are graphitisable carbons. Their microstructure is a mixture of optical texture of various sizes, from the optically isotropic to domain and flow anisotropy. Only short range order associated with non-graphitic carbons, usually exists at the crystallographic level. Various types of cokes are raw (green) coke, calcined coke, petroleum coke, metallurgical coke, delayed coke, needle coke and coal-derived pitch coke[40].

3.1 PROCESSING OF THE INTERMEDIATE PITCH INTO A GREEN COKE POWDER

About 200–300 g portion of the intermediate pitch was taken in a stainless steel boat, which was placed inside a stainless steel reaction vessel having a provision for flow of an inert gas (nitrogen) into it. The reaction vessel containing the sample was kept in an electrically-operated muffle furnace which was gradually heated to the desired temperature in the range of 450–550 ℃ with the help of a microprocessor-based programmable temperature controller for a period of 1–5 h, while maintaining a flow of nitrogen gas inside the reaction vessel. The rate of heating is adjusted so as to allow the polymerisation and dehydrogenative condensation reactions between the molecules to take place. During this heat-treatment, low / medium molecular weight components as well as various reaction products are eliminated as volatiles and the pitch solidifies to coke, called as the 'green coke'. This green coke was then taken out of the boat for further processing[41].

3.2 HEAT-TREATMENT OF THE INTERMEDIATE PITCH TO OBTAIN A GREEN COKE

About (300g or 2500g) portion of the intermediate pitch was taken in a suitably designed stainless steel vessel having a provision for flow of an inert gas(nitrogen) into it. The reaction vessel containing the intermediate pitch sample was kept in an electrically-operated muffle furnace which was gradually heated to the desired temperature in the range of 470-480°C with the help of a microprocessor-based programmable temperature controller for a period of 3–4 h while maintaining a flow of nitrogen inside the reaction vessel. The rate of heating was so adjusted as to allow the polymerisation and dehydrogenative condensation reactions between the molecules to take place. During this heat-treatment, low / medium molecular weight components as well as various reaction products were eliminated as volatiles and the pitch solidifies to coke, called as the 'green coke'. This green coke was then taken out of the vessel for further processing[41].

3.3 PULVERISATION OF THE GREEN COKE INTO A FINE POWDER

The green coke was first crushed into a powder using pestle and mortar or an edge-runner grinder. It was then ground into a fine powder using a ball mill with steel ball (available with party) or a centrifugal ball-mill (available with NPL) having the jar (bowl-type) and the balls both made up of 99.9% purity alumina. The jar was rotated for a period of 5–8 h or higher as to obtain the green coke powder having a mean size of around 5–10 µm. The material was then taken out of the jar and is then characterised for quinoline and toluene insoluble contents and coking value, volatile matter etc[41]

3.4 MODIFICATION OF THE GREEN COKE POWDER

The values of quinoline and toluene insoluble contents of a good green coke finely ground powder were observed to be QI=95.0-97.5%, TI=96.0-98.5%, and CV=89-91% respectively. In a green coke powder, if the values of QI and TI were lower than above mentioned values , the product obtained from the powder would show swelling and / or cracks upon carbonisation, while if the QI–TI values were higher than these, the resultant carbonised product would be weak and have inferior characteristics. However, the problem of low QI–TI was overcome by subjecting the powder to a modification (oxidation) treatment in the presence of air at a temperature in the range of 150–220℃ for a suitable period of time. Alternatively, extraction with suitable solvents such as tar-based oil, toluene etc. could also be done to modify the green coke. It was also observed that the extraction treatment was found to be more suitable for the modification of green coke powder. This treatment resulted in an enhancement in the values of QI and TI such that the product made from the modified green coke powder then leads to a crack-free, dense and strong product on carbonisation / graphitization[41].

The green coke prepared as above is used for the development of many advanced carbon products such as high thermal conductivity graphite, carbon ceramic composites and carbon based composites.

4.0 COMPOSITES OF CARBON MATERIALS

The composites are materials composed of at least two different materials, each having its own typical properties. The composites utilize the superior properties of both materials. The conventional composites are granular or particulate type but the modern composites are mostly fibre reinforced based. The two examples of granular composites of carbon are graphite crucibles and metal impregnated carbon brushes. The graphite crucibles are made from natural graphite as filler and ceramic/ carbon as binder. The natural graphite gives high thermal conductivity to the graphite crucibles whereas ceramic/ carbon binder provides the necessary strength and thermal stability. The metal impregnated brushes on the other hand have polycrystalline/ natural graphite which provides good electrical and thermal conductivity whereas the metals improves the electrical conductivity further.

In the fibres based composites employing carbon fibres, carbon fibre are used as reinforcing materials. Carbon fibres are a new breed of high strength materials which are stronger than steel, stiffer than titanium and lighter than aluminium. They can be reinforced on the plastic matrix (epoxy, polyester, polyamide, etc.) to obtain so called fibre reinforced plastics. The use of CFRP is however restricted to 250^{o}C because plastic material starts degrade about such temperatures. The carbon fibres can be reinforced on a carbon matrix to obtain carbon fibre reinforced carbon composites or simply carbon-carbon composites which can be used to upto 3000^{o}C in non-oxidizing/ protective atmospheres. Similarly carbon fibres can be reinforced in a metal, ceramic, glass and concrete matrix to obtain carbon fibre reinforced metal/ ceramic/ glass or concrete composites respectively. In these composites, the properties of carbon fibres and the matrix materials are utilized to the maximum advantage.

4.1 CARBON-CARBON COMPOSITES

Carbon-carbon (C-C) composites consist of a carbon fiber reinforcement of a carbonaceous matrix. Carbon fibers are produced from a variety of precursors including pitch, polyacrylonitrile (PAN), vapor grown, and rayon. The matrices used in C-C composites are derived from resins, pitches (coal-tar or petroleum) and chemical vapor infiltrated (CVI) carton, as well as hybrids of these. The carbon composites can also be prepared using granular carbon materials like green coke and graphite.

The variety of structures displayed by carbon fibers and carbon matrices provide for a wide range of properties (mechanical and physical) in the final product. In addition, interactions between the carbon fibers and the matrix carbons play an important role in determining the properties of the compositeramic composites and carbon based composites[42].

4.2 FABRICATION METHODS

All fabrication methods for carbon-carbon composites are based on various combinations of the pyrolysis methods:

1. *One Step Pyrolysis:* The first fabrication process for carbon-carbon composites was the so called HITCO process. Textiles from rayon were pyrolyzed in hydrocarbon atmosphere. This process is a combination of a solid state pyrolysis of the rayon textile resulting in a carbon fiber framework and gas phase pyrolysis (GPP) of hydrocarbon vapor for formation of the pore filling matrix or chemical vapour deposition (CVD). The process developed for tip cones of missile is still used, but in very limited volume only.
2. *Two Step Pyrolysis:* First, solid state pyrolysis of carbon fiber precursor to carbon fiber in solid state and secondly, gas phase pyrolysis of evaporated hydrocarbons in an autoclave to form the carbon matrix. This process is widely used to day, and also applied not only for missile technology but also for carbon-carbon disk brakes. The process involves high investment costs and high residence times for the substrate within the autoclaves (in the order of one month). It is only economic if the respective equipments are already available from most former military productions.
3. *Three Step Pyrolysis:* This process is a modification of the process described earlier. Pre-carbonization or-carbon precursor fibers hy solid state pyrolysis, formation of carbon fiber framework by binding with a phenolic, pyrolysis of this

binder precursor into a porous bulk carbon-carbon material and subsequent impregnation by chemical vapor deposition to fill the pores by pyrolytic carbon or graphite.

4. *Multi Step Pyrolysis:* First steps, as have been described above in process' No.3, are the same, namely carbonization of the carbon fiber precursor; formation of a fiber framework by means of a temporary binder mostly a phenolic, but after carbonization pore filling by a liquid impregnation step with the help of phenolic precursor polymer or pitch to repeated reimpregnation and recarbonization up to seven times. In case of pitch as a liquid carbon precursor for pore filling, high pressure pyrolysis is applied to get a high carbon yield up to 60% instead of less than 50% if carbonized without pressure. The need for pressure carbonization can be avoided by the use of additives.
5. *Prepreg-processes in the Form of Stick (Rod): Stick or of Tape-like Prepregs:* arrangement and the carbon fibers are embedded in prepolymers of a thermosetting resin. In case of rod-like prepregs the stick-frame can be impregnated before first carbonization during which the prepreg sticks and the matrix precursor are pyrolyzed simultaneously. In case of tapelike prepregs the stilplesof prepreg sheets are pyrolyzed before further densification (impregnation and re-carbonization) steps. For both alternatives the geometrical process variations are of greatest importance[43].

4.3 MATRIX CONTROL IN CARBON-CARBON COMPOSITES

For the production of C-C composites various problems such as selection of carbon fibers, their way of weaving, selection of matrix precursor, structure and texture control in the matrix carbon etc. are to be looked into. Here we consider the matrix control in C-C composite in relation to their formation, structure and texture of various carbon materials.

Two factors have to be controlled in the matrix of C-C composites, that is density and texture. These two factors, that is, to get high density and to control the texture of matrix, carbon strongly depend upon the production .process. Two processes have been employed, impregnation with resin, including pitches and infiltration of carbon deposit by pyrolysis of hydrocarbon gases. In the former process, repetition of impregnation and carbonization is essential to get high density in matrix carbon. Therefore, the selection of resins in relation with their carbonization behaviour (carbon yield after carbonization, texture of resultant carbon etc.) is very important to control the matrix in carbon-carbon composites.

Carbonization under pressure was found to be quite effective to obtain high value carbon yield and also to control the texture of the resultant carbon. Mixing of different kinds of precursors give different textures of resultant carbons[44].

4.4 ROLE OF MATRIX IN COMPOSITES

In choosing to reinforce an engineering material we are effectively selecting the matrix a composite. This matrix is required to perform several functions, most of which are vital to the satisfactory performance of the composite. Bundles of fibers or aggregates of particulate matter are in themselves, of relatively little use to an engineer, no matter how strong or rigid the individual may be and it is only the presence of matrix or binder that enables us to make use of them. The roles of matrix in fibre reinforced and particulate composites are quite different.

The binder for particulate aggregate simply serve to retain the composite mass in a solid form but the matrix in a fiber composite perform a variety of other functions which characterize the behaviour of the composite. The matrix binds the fibers together, holding them aligned in the important stress direction. loads are applied to the composite, are them transferred into the fibers, which constitute the principal load bearing component, through the matrix, enabling the, composite to withstand compression, flexural and shear forces as well as tensile loads. The. ability of composites reinforced with short or chopped fibres to support load of any kind is exclusively dependent on the presence of matrix as the load transfer medium and the efficiency of this transfer depends on the quality of the fiber-matrix bond.

The matrix must isolate the fibres, so that they can act as separate entities. Most reinforcing fibers are composed of solids which are brittle and of which the strength is therefore, highly variable. When such materials are used in the form of an aggregate of fine fibers, not only are the fibers stronger than the monolithic form of the same solid but also there is the additional benefit that the fiber aggregate does not fail catastrophically. The fiber bundle strength is less variable than that of a monolithic rod of equivalent load bearing ability. But these advantages of the fiber aggregate can only be realized if the matrix separates the fibers from each other so that cracks are unable to pass unimpeded through sequences of fibers in contact.

The matrix must protect the reinforcing filaments from mechanical damage (e.g., abrasion) and from environmental attack. Since most resins which are used as matrices for glass fibers permit diffusion of water and the environmental damages that results is aggravated by the presence of stress. In cement the alkaline nature of the matrix itself is damaging to ordinary glass fibers and it is necessary to develop alkali resistant glass to counter this. For composites operating at elevated temperature, the matrix should protect the fibers from oxidative attack.

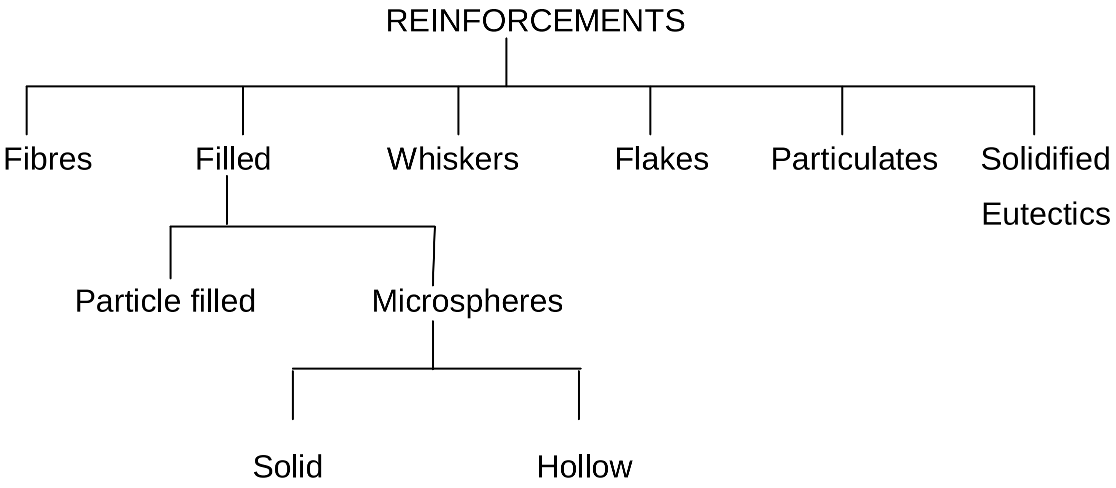
A ductile matrix will provide a means of slowing down or stopping cracks that might have originated at broken fibers. Conversely, a brittle matrix may depend upon the fibers to act as matrix crack stoppers.

Through the quality of its grip on the fibers, manifested most directly in the interfacial bond strength, the matrix can be an important means of increasing the toughness of the composite. The potential for reinforcing any given material will clearly depend to some extent on its ability to carry out some or all of these matrix functions, although. there are often other considerations. The question of density is particularly important. For structural applications involving compression or flexural design loads. the Young's Modulus, E and density ratio as E/p2 or E/p3 is important factor[45].

4.5 REINFORCEMENTS

The solid, another constituent of composites that has higher strength and more rigidity, is reinforcement. It can be fiber, fabric particles, particulates or whiskers. Fibers are essentially characterized by one very long axis and other two axes either often circular or near circular; particulates have no preferred orientation and so does their shape. Whiskers have preferred shape and small both in diameter and length as compared to fibers but are defect free.

Different types of reinforcements used in composites are following:



Reinforcing constituents in composites provide the strength but they also serve certain additional purpose of heat resistance or conduction, resistance to corrosion and provide rigidity.

Reinforcement that gives the matrix strength must be stronger and stiffer than matrix and capable of changing failure mechanism to the advantage of composite. This means that ductility should be minimum or even nil and the composite must behave as brittle as possible. A wide variety of fibers are available for use in composites. The most commonly used fiber in polymer matrices are various types of carbon$_1$ glass and aramid (kevelar) fibers. The unique combination of properties available in the fibers provide the outstanding structural characteristics of fiber reinforced composites. Fibers can be used in many forms, which can differ in amount of fiber, fiber type, fiber length, orientation and fiber hybridization gives several examples of possible combinations.

Predictions of composite strength and stiffness as a function of constituent properties can be made. To a first approximation, composite tensile properties in fiber direction (L) can be predicted by a rule of mixtures based on fiber (f) properties, neglecting matrix contribution. Thus

$$E_L = E.V_f \text{ and } F_L = F.V_f$$

E, F and V_f *refer* to modulus, strength and fiber volume fraction respectively. Strengths and stiffness are in the direction normal to fiber are much less. Advanced composites are anisotropic with strength, stiffness and toughness as a function of direction relative to that of fiber. Anisotropy is main difference between advanced and structural composites[46].

4.6 Typical Characteristics of C-C Composites

. Light weight and low density

. High strength and .stiffness

. Low thermal expansion (thermal expansion coefficient is low)
. High thermal conductivity, decreasing with increase in temperature . High thermal shock resistance
. High fracture and creep resistance
. Pseduo-plastic behavior
. Good fatigue resistance
. Corrosion resistance

4.7 APPLICATIONS OF CARBON-CARBON COMPOSITES

The most impressive display of C-C composites as high temperature materials with high resistivity against thermoshock are the nose cap and the leading edge in the US space shuttle where in the phase of re-entering the earth atmosphere temperature up to 1500℃ can arise. Also aircraft brake components are made from C-C composites. .

A newer application is that for heating elements, heat exchanger tubes for helium cooling in high temperature reactors. Moulds for heat forming metals (super plastic mould at lOOO℃), screw made of 2-dimensi onal C-C composites the unique challenge is the development of materials for Oriental Express, Which can cover distance between America and Asia in three hours[47].

4.7.1 APPLICATION OF CFRC AS BIO-MATERIAL

Carbon fiber is .an excellent bio-material. Medical equipment application of CF include, X-ray table tops, scanner cradles, couches, stretchers, and film cassettes, The fiber is also used to produce thermoplastic composites for orthopaedic implants, CFRC has been used to produce artificial heart valves, Steinmann pins and artificial hip prostheses. The major advantage of carbon is its bio-compatibility. Different applications of CFRC.

1. CFRP	
* non-tissue contact applications	X-ray table tops, cradles, scanners, couches, stretchers.
* orthotic etc.	Frames, braces, splints, cones etc.
* implantable reinforcement CF, matrix UHMWPE, polysulphone, epoxy	Bone plates, hip prostheses (UHMWPE) polysulphone matrix
2. CFRC	Orthopaedic implant, artificial heart valves
3. CF	Ligament and tendon repairs

Different applications of CFRC

CFRC is used in two group of "applications, firstly the application in apparatus and secondly the application as implant material. In the first group, chair made from CFRC, which has enormously light weight. In second group, the application of CF as ligament replacement at human knee, human hip joint replacements. Thus carbon fibers as the back-bone"' of new revolutionary material are available to day In high performance, quality.

4.7.2 APPLICATIONS IN AEROSPACE

Light mass structures are preferentially needed in aerospace applications. US space shuttle consists in main parts CF reinforced epoxy resins (cargo bay doors. and booster rocket casings). Modem commercial aircraft use carbon fiber reinforced composites instead of aluminium. There are already airplanes in development where whole structure consists of composites instead of metals. Inner parts of airplanes are replaced by advanced composites, for example. the columns supporting the floor panels or the seats for passengers.

4.7.3 APPLICATIONS IN TRANSPORTATION

Because of the requirements for the replacement of metals in primary structures of airplanes and based on the years long critical tests, the quality of CFRC and their processing have been improved. Automobile industry can take advantages in using this experience in replacing various metal parts in the cars. It seems today, that parts of the outer structure will be fabricated by CFRCs. Highest chances for advanced composites are given at the moment to leaf springs, drive shafts, parts of frames, and other parts where higher stiffness is needed. In racing cars such structural elements are already in practical use. One can assume that all leading automobile manufacturers are mostly interested to use advanced composites as part of the engines. Information in this regard is secret because of commercial practices.

Further development for transportation purpose is transportable bridges with 40 meter length. It has been designed for vehicles up to 66 tones weight. All leading carrying structural elements are made from uni-directionally carbon reinforced epoxy. Thus achieving a meter weight of the bridge only 500 kg.

4.7.4 APPLICATION IN MACHINERY AND APPARATUS

The successful application for turbine blades, compressor blades, windmill blades, ultracentrifuges, flywheels, and in other machines has been proved. In off shore drilling, the new application can be mentioned, these are lightweight outer tapes for off shore equipment. In this application high corrosion resistance advanced composites are required.

4.7.5 APPLICATIONS IN CRYOGENICS

Materials for cryogenic temperatures require some other combination of properties than for conventional temperatures. Especially, the disadvantageous embrittlement of metallic materials at low temperature is mentioned. CFRC are most suitable for applications at cryogenic conditions, because

I. The room temperature strength properties remain unchanged even at lowest temperature.

2. The inter_laminar shear strength in polymer matrix composites improve with lowering of temperature.

3. Carbon fibers have good thermal and electrical conductivity.

These transport properties disappear at lowest temperature because of the contribution by electrons is completely eliminated. These properties offer promising applications in pulsed I superconductive electromagnets. For this application, carbon fibers as substrate for superconducting niobium carbonitride layers are in the development stage.

5.0 CHRACTERIZATION METHODS

5.1 EXPERIMENTAL TECHNIQUES USED FOR CHARACTERISATION

The following are the methods for the characterisation of coal tar and petroleum pitches and their blends, green cokes and composites.

5.1.1 DETERMINATION OF SOFTENING POINT (SP)

The softening point of the pitches was measured either by the Ring and Ball Method, in accordance with ASTM-D-2398 specifications, or by the Mettler Method, as per the ASTM-D-3104 / DIN 51920 specifications. The same are described in the following sub-sections.

5.1.1(a) DETERMINATION OF RING AND BALL SOFTENING POINT

The Ring and Ball softening point is defined as the temperature at which a disc of the sample held within a horizontal ring is forced downward a distance of 2.54 cm under the specific weight of a steel ball, as the sample is heated at a prescribed rate in water or glycerine bath. It covers a softening point range of 30–230 ℃.

A portion of the sample is heated until it has become sufficiently liquid to pour, the temperature to be raised by no more than 75 ℃ above the anticipated softening point. The sample is poured into two rings preheated to the pouring temperature. While filling, the rings should rest on an amalgamated brass plate. After cooling to room temperature, the excess material is trimmed off with a heated spatula or knife. Should it be necessary to repeat the process, a fresh sample and clean rings are mandatory. Centering guides are used to place the balls on the specimen, and the assembly is placed in a bath filled with distilled water or glycerin, to a depth of not less than 10 cm and not more than 10.6 cm. The temperature of bath is maintained at 5℃ for 15 minutes. The temperature is raised at 5 ± 0.5 ℃ / min. The temperature observed at the instant the sample surrounding the ball touches the bottom plate, placed 2.54 cm below the ring holder, is recorded as the softening point. If the difference between the values obtained for the two specimens exceeds 1℃, the test should be repeated.

5.1.1(b) DETERMINATION OF METTLER SOFTENING POINT

The Mettler Softening Point of a material is defined as the temperature at which a softened sample of the material, taken in a standard softening point sample cup, flows 20 mm out of 6.35 mm diameter opening, on slow heating. The Mettler Softening Point Apparatus consists of a Cartridge Assembly comprising a Cup Holder and a Cylindrical Sample Cup with 6.35 mm diameter orifice and a collector sleeve, which is placed in a Measuring Cell (FP 83) surrounded by a small electrically-heated cylindrical furnace, as schematically shown in Fig.17.

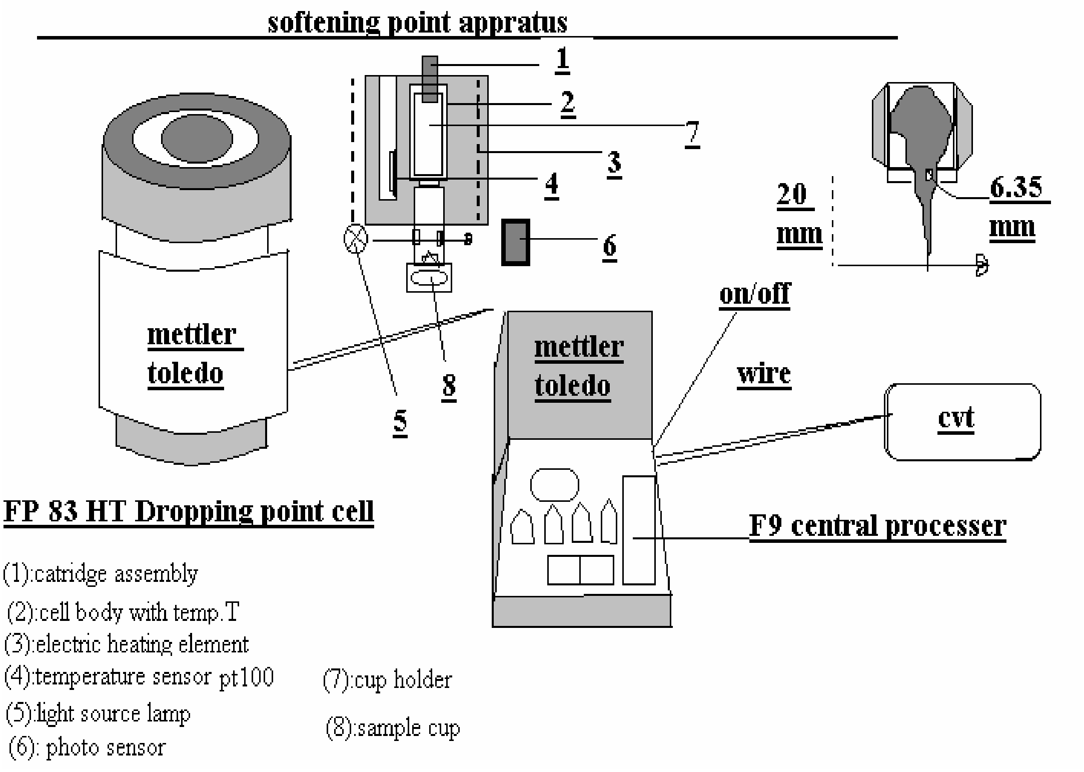


Fig. 17: Schematic diagram of Mettler softening point apparatus

The test material, taken in the sample cup placed over the cup holder in the cartridge assembly, is heated in the Measuring Cell inside the electric furnace at a rate of 2 °C / min. The temperature at which the first drop of the sample obstructs the light beam placed 20 mm apart from the bottom of the sample is detected by a photoelectric sensor kept inside the Measuring Cell, and displayed on the Central Processing Unit (FP 90) of the Mettler Softening Point Apparatus, as the softening point of the test material.

5.1.2 DETERMINATION OF COKING VALUE (CV)

A sample of the pitch is pyrolysed for a specific time at a specified temperature in an equipment that limits the oxygen supply. A 1–2 g of sample of the dried pitch is weighed in a quartz crucible and placed in a quartz glass or stainless steel reaction vessel having a provision for flowing of high purity nitrogen gas. The quartz assembly is then placed in an electrical muffle furnace, the temperature of which is gradually raised to 950 °C at a rate of 200 °C / h and maintained at 950 °C for 30 minutes and then cooled to room temperature. The crucible is then weighed to get the weight of the coke. From these observations, the coking value is calculated as the residue percent weight of the sample taken.

5.1.3 DETERMINATION OF ASH CONTENT

The amount of sample to be ashed depends upon the anticipated ash content of the material and any subsequent analysis to be conducted on the ash. A minimum of 10 mg of ash is generally required. A suitable quantity of the representative dried sample is weighed out in an ignited crucible (porcelain, silica, or platinum) on an analytical balance. The crucible is then carefully heated in an electrical muffle furnace to 950°C for 30 minutes. When all the carbon has been combusted, the crucible is cooled and weighed again. The ignition at 950 °C is repeated until a constant weight is obtained. From these observations, the ash content is calculated as the residue percent weight of the sample taken.

5.1.4 DETERMINATION OF QUINOLINE INSOLUBLE CONTENT (QI)

To determine the quinoline insoluble content of a pitch, about 1 g of the sample is digested with 30 ml of the distilled quinoline at 70 ℃ for half an hour. The pitch, is first crushed, ground and sieved to obtain a (–30 B.S. mesh) powder which is then used for the sample. It is then rapidly filtered with suction in a grade-4 sintered glass crucible. The residue is then washed with small portions of toluene and acetone successively, after which the crucible is dried at 110 ℃ in a drying oven. After cooling, it is weighed to get the quinoline insoluble content.

5.1.5 DETERMINATION OF TOLUENE INSOLUBLE CONTENT (TI)

To determine the toluene insoluble content of a pitch, about 1 g of the sample is accurately weighed and digested with 30 ml of toluene at 90–100 ℃ for half an hour. The material is first crushed, ground and sieved to obtain a (–30 B.S. mesh) powder which is then used for the sample. It is then rapidly filtered with suction in a grade-4 sintered glass crucible and subsequently washed with small portions of acetone. The crucible is then dried at 110 ℃ in an oven. After cooling, it is weighed to get the toluene insoluble content.

5.1.6 DETERMINATION OF SPECIFIC GRAVITY (SG)

A fragment weighing 5–20 g of the pitch is suspended by a thin synthetic fibre from an analytical balance and its weights, both in air and in distilled water, at a particular temperature are determined. The specific gravity is then calculated from the relationship,

$$\text{Specific gravity} = a / (a-b)$$

where, a and b are the weights of the specimen in air and in distilled water, respectively.

5.2.0 EXPERIMENTAL TECHNIQUES USED FOR CHARACTERISATION AFTER HEAT TREATMENT (HTT)

The characterisation of the green or carbonised (HTT~1000 ℃) or graphitised (HTT ≥ 2500℃) product was done with respect to apparent (bu lk) density, weight loss, linear and volume shrinkages, specific gravity, kerosene density, open porosity, ash content, electrical resistivity, bending strength, Shore hardness, and optical / scanning electron microscopy, as per the procedures described in the following sub-sections.

5.2.1 DETERMINATION OF APPARENT / BULK DENSITY

The apparent (bulk) density of a green carbonised or graphitised product is determined from the measurements of its mass and dimensions as the ratio of its mass to its volume.

5.2.2 DETERMINATION OF WEIGHT LOSS (WL)

The weight loss in a green carbon upon carbonisation (HTT ~1000 °C) or graphitisation (HTT ≥ 2500 °C) is obtained by the following expression:-

$$\text{Weight loss (\%)} = [w/W] \times 100$$

where, W = weight of the green carbon, and

w = reduction in weight of the green carbon upon carbonisation / graphitisation.

5.2.3 DETERMINATION OF VOLUME SHRINKAGE (VS)

The volume shrinkage in a green carbon upon carbonisation (HTT=1000 °C) or graphitisation (HTT=2500°C) is determined knowing the volumes of the green carbon in the green and carbonised/ graphitised states. It is given by the expression:

$$\text{Volume shrinkage (\%)} = (v/V) \times 100$$

where; V = volume of the green carbon, and

v = reduction in volume of the green carbon upon carbonisation / graphitisation.

5.2.4 DETERMINATION OF LINEAR SHRINKAGE (LS)

The linear shrinkage in a green carbon upon carbonisation (HTT~1000 °C) or graphitisation (HTT~2500°C) is determined knowing the lengths of the carbon in the green and carbonised / graphitised states. It is given by the expression:

Linear shrinkage (%) = (l/L) x 100

where, L = length of the green carbon, and
l = reduction in length of the green carbon upon carbonisation / graphitisation.

5.2.5 DETERMINATION OF SPECIFIC GRAVITY (SG)

A fragment weighing 5–20 g of the pitch is suspended by a thin synthetic fibre from an analytical balance and its weights, both in air and in distilled water, at a particular temperature are determined. The specific gravity is then calculated from the relationship,

Specific gravity = a / (a–b)

where, a and b are the weights of the specimen in air and in distilled water, respectively.

5.2.6 DETERMINATION OF ELECTRICAL RESISTIVITY (ER)

The electrical resistivity of the specimen of a carbonised or graphitised product is determined by passing a suitable current across the cross-section of the specimen placed between two thick copper or brass plates and measuring the potential drop across a known distance along the length of the specimen with the help of a micro voltmeter using two probes. The electrical resistivity is then easily obtained from the following equation:

$$\rho = \frac{V \cdot A}{I \cdot L}$$

where, p = resistivity of the test-specimen (Ohm cm)
V = potential drop across the probe pins (volt)
A = area of cross-section of test-specimen (cm^2)
I = magnitude of d. c. current (Ampere)
L = distance between the probe pins (cm)

5.2.7 DETERMINATION OF BENDING STRENGTH (BS)

The Instron Universal Testing Machine, Model 4411, was used to determine the bending strength of the carbonised or graphitised products. The test-specimen is kept on two knife edges to hold the specimen tightly. A slowly increasing load is applied on the specimen at a cross-head speed of 0.5 mm/min through the middle knife edge till the specimen breaks. Stresses so developed in the test are measured with the help of a load cell and recorded on a chart. The vertical movement of the chart corresponds to the deflection in the specimen. Thus, a load versus deflection plot of the specimen is obtained. The bending strength is then calculated as follows:

$$\text{Bending strength} = (3\, P_{max} \,.\, S) / (2\, b\, t^2)$$

where, P_{max} = maximum load at which the test-specimen breaks,

S = Span length (usually 30 mm),

b = width of the test-specimen, and

t = thickness of the test-specimen.

5.2.8 EXAMINATION OF MICROSTRUCTURE BY OPTICAL MICROSCOPY

The optical microscopic examination of the pitch or pitch-based fibres was done on the Leitz Mettaloplane Optical Microscope. The first step in the microscopic examination was the preparation of the sample, which was done in the following manner.

The test material was taken in a cylindrical plastic or glass capsule (approx. 25 mm diameter and 15 mm height), and a freshly prepared epoxy or polyester resin is poured over the material such that it just covers the specimen. After the resin has partially set, more of it was poured over the specimen to fill the capsule completely. The whole system was allowed to stand at room temperature till the resin was completely set. The mounted specimen was then removed from the plastic capsule and its surface was first ground manually on a silicon carbide water-proof cloth with grit size varying successively from 200 to 800, using tap water. Subsequently, the mounted specimen was polished on a lapping machine using alumina powders of size varying from 1 µm down to 0.05

µm, after which the sample was washed under tap water and finally in an ultrasonic cleaner using water to remove off any sticking alumina particles. The mounted specimen was then dried in air to make it ready for the microscopic examination. The specimen was observed for the microstructure under crossed polarisers and a photograph of the microstructure (micrograph) was obtained using the camera attached to the microscope.

5.2.9 DETERMINATION OF THERMAL CONDUCTIVITY

The thermal conductivity of the specimen of a carbonized or graphitized product is determined by making use of the following empirical relation[49] :

$$K \times p = 1296$$

or

$$K = 1296 / p$$

Where, K = thermal conductivity (W / mk)

p = electrical resistivity (µ Ω m)

6.0 DEVELOPMENT OF CARBON COMPOSITES FROM PITCH BASED AND SYNTHETIC GRAPHITE

Four batches of carbon based composites incorporating 0, 15, 30 and 45 % of finely-ground synthetic graphite (mean particle size = 5.5 µm) were prepared from a coal tar pitch with its characteristics shown in Table–5, using the process developed by us at NPL, the block diagram of which is shown in Fig.18.

Accordingly, a coal tar pitch of characteristics shown in Table–4 was heat-treated at 520 °C for 45 min. in the presence of 0, 15, 30 and 45 % (by weight of) of finely-ground synthetic graphite with a view to obtain green cokes based composites of improved thermal conductivity. These green cokes were ball-milled to fine powders in a centrifugal ball-mill and then solvent-extracted to obtain their modified powders. The characteristics of resulting plates at both

TABLE–4

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH AND THE RESULTING GREEN COKE

S. No.	CHRACTERISTICS	PRECURSOR COAL TAR PITCH	GREEN COKE
1.	Softening point (°C)	79.0	–
2.	Specific gravity	1.27	–
3.	Quinoline insoluble content (%)	0.0	95.6
4.	Toluene insoluble content (%)	15.6	97.2
5.	Coking yield (%)	43.7	91.8

carbonised as well as graphitised levels [48] are shown in Table–5. Besides this, the precursor pitch, green coke obtained from it and the carbonised plates of different batches were subjected to optical microscopy and the micrographs obtained are shown in Figs. 19 and 21.

It is seen from Table–5 that the introduction of synthetic graphite (up to 45%) increases gradually the green density of the composite plates from 1.32 to 1.54 g cm^{-3}. This increase of green density with the increase in the content of synthetic graphite is due to the higher density of the synthetic graphite compared to the green coke in the green mixture.

Further, the weight loss is seen to decrease continuously from 7.2 to 4.6 % at a HTT of 1000 °C and 9.4 to 6.1 % at 2600 °C as the synthetic graphite content in the composite plates increases from 0 to 45%. This is because of the decreasing content of green coke with the increasing content of the synthetic graphite in the green coke - synthetic graphite composite mixture (GC–SG), as it Is only the green coke part of the mixture which is undergoing weight loss in the form of volatiles, the synthetic graphite being already heat-treated to around 2600 °C will have no weight loss up to 2600 °C. The volume shrinkage and the linear shrinkage, in turn, are observed to decrease continuously from 27.8 to 15.9 %

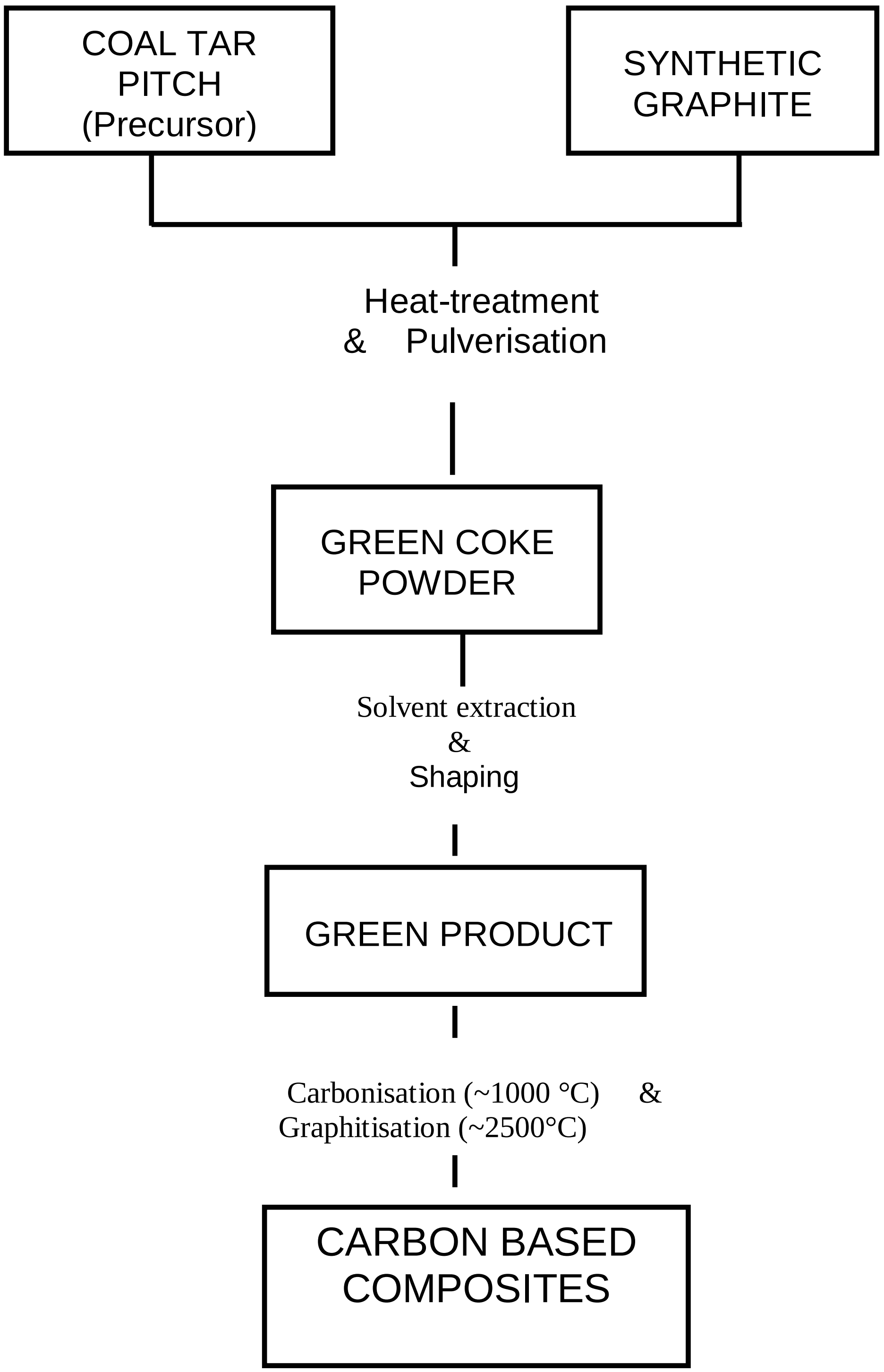


Fig.18: **Flow-diagram of process for the production of carbon based composites from green coke incorporating synthetic graphite.**

TABLE– 5

SUMMARY OF THE CHARACTERISTICS OF GREEN COKE BASED COMPOSITE PLATES (HTT = 1000/2600℃) HAVING 0–45% OF SYNTHETIC GRAPHITE BY WEIGHT OF PRECURSOR COAL TAR PITCH

S. No.	CHARACTERISTICS	PERCENTAGE OF SYNTHETIC GRAPHITE BY WEIGHT OF PRECURSOR COAL TAR PITCH			
		0	15	30	45
1.	Green density (g cm^{-3})	1.32	1.41	1.47	1.54
2.	Weight loss (%)	7.2 (9.4)	6.7 (8.6)	5.7 (7.2)	4.6 (6.1)
3.	Volume shrinkage (%)	27.8 (35.6)	22.5 (29.7)	20.0 (24.6)	15.9 (19.4)
4.	Linear shrinkage (%)	10.0 (12.7)	8.2 (10.2)	7.0 (8.5)	5.7 (6.6)
5.	Density amplification Factor	1.285 (1.407)	1.204 (1.300)	1.179 (1.231)	1.134 (1.165)
6.	Bulk density (g cm^{-3})	1.69 (1.86)	1.70 (1.84)	1.73 (1.82)	1.74 (1. 80)
7.	Kerosene density (g cm^{-3})	1.90 (2.17)	1.92 (2.17)	1.96 (2.20)	2.00 (2.21)
8.	Open porosity (%)	11.1 (14.3)	11.5 (15.2)	11.7 (17.3)	13.0 (18.6)
9.	Bending strength (MPa)	78 (68)	74 (61)	66 (56)	59 (46)
10.	Young’s modulus (GPa)	15.1 (8.7)	14.1 (8.3)	12.6 (8.1)	12.6 (7.8)
11.	Shore hardness	69 (66)	73 (65)	68 (64)	66 (61)
12.	Electrical resistivity (mΩcm)	4.5 (1.45)	3.4 (1.23)	3.0 (1.17)	2.5 (1.23)
13.	Thermal conductivity* (W/mK)	29 (89)	38 (105)	43 (111)	52 (105)

NOTE : 1. Density Amplification Factor = $\dfrac{\text{Fractional residual weight}}{\text{Fractional residual volume}}$

2. The Figures in parentheses refer to the values at a HTT of 2600 ℃.

3. * refers to estimated values.

and 10.0 to 5.7 %, respectively, at a HTT of 1000 °C, and from 35.6 to 19.4 % and 12.7 to 6.6 %, respectively, at 2600 °C, as the synthetic graphite content in the green composites increases from 0 to 45 %. This again is due to the fact that it is basically the green coke part of the green coke - synthetic graphite composite which actually undergoes shrinkage, the synthetic graphite part being already heat-treated to 2600 °C or so, will not have any shrinkage up to 2600 °C.

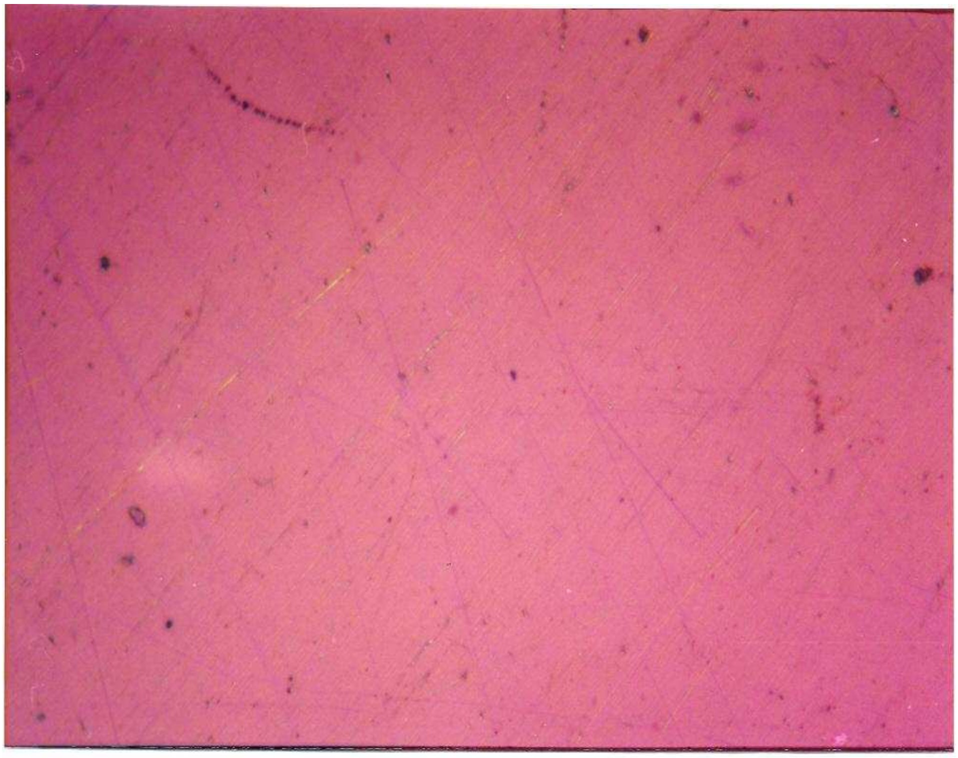
The overall or resultant effect of weight loss and volume shrinkages as a result of heat-treatment has been termed as the ‘Density Amplification Factor (DAF)’ which is defined as the ratio of fractional residual weight to fractional residual volume of the plates upon the heat-treatment. Accordingly, we see that the DAF goes on decreasing with the increase in the synthetic graphite content in the green coke - synthetic graphite mixture from a value of 1.285 to 1.135 at 1000 °C and from a value of 1.407 to 1.165 at 2600 ° C. The net result is that inspite of the significant and gradual increase in the green density of the composite plates as the synthetic graphite content increases from 0 to 45 %, we have a nominally increasing value (1.69 to 1.74 g cm^{-3}) of the composite plates at a HTT of 1000 °C and a slightly decreasing value (1.86 to 1.80 g cm^{-3}) at a HTT of 2600 °C because of the decreasing value of DAF at both 1000 °C and 2600 °C.

Furthermore, it is seen from Table–5 that the kerosene density of the plates at both the HTTs, 1000 °C as well as 2600 °C, is always higher than the bulk density at these temperatures, which implies that there is some amount of porosity in the plates of all the batches at both these HTTs. Accordingly, we see that the open porosity goes on increasing with the increase in the synthetic graphite content in the green coke - synthetic graphite mixture, and attains values of 11.1–13.0 % at a HTT of 1000 °C and 14.3–18.6% at 2600 °C . The bending strength, in turn, goes on decreasing with the increase in the synthetic graphite content at both the HTTs, 1000 °C as well as 2600 °C, thus attaining values of 78 to 59 MPa at 1000 °C and 68 to 46 MPa at 2600 °C. These variations in the bending strength of the plates may be attributed to increasing open porosity in the plates at both the HTTs. The Young's modulus is seen to decrease from 15.1 to 12.6 GPa at 1000 ℃ and from 8.7 to 7.8 GPa at 2600 ℃, whereas the Shore hardness varies in a narrow range of 66–73 at 1000 ℃ and 61 – 66 at 2600 ℃. The higher values of Young's modulus and Shore hardness at a HTT of 2600 ℃ compared to a HTT of 1000 ℃ may be due to the presence of a more cross-linked structure and a smaller size of the crystallites at a HTT of 1000 ℃ compared to a relatively cross-linked structure and a higher crystallite size at a HTT of 2600 ℃.

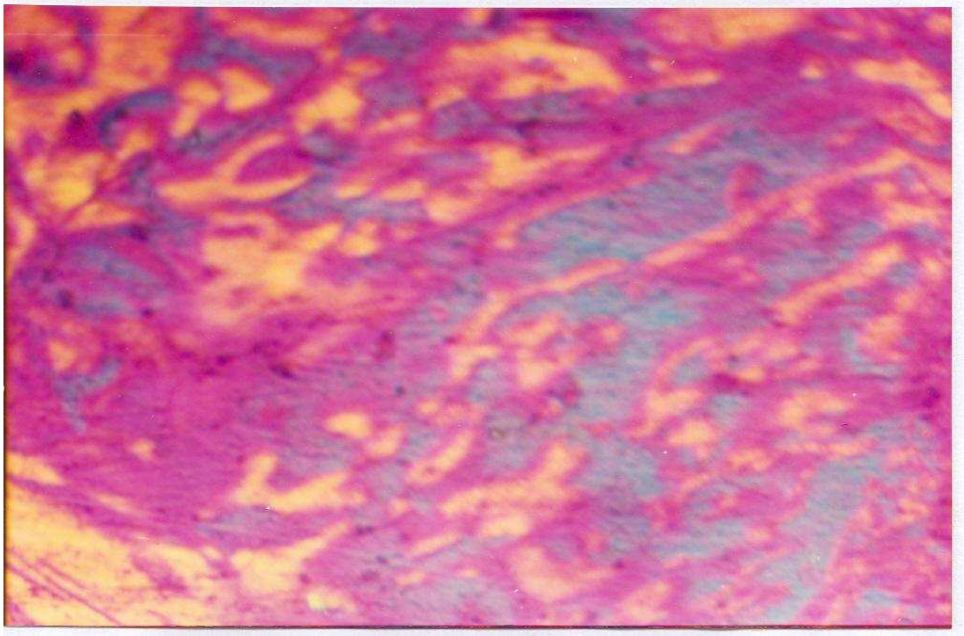
The electrical resistivity of the composite plates is seen to decrease gradually from 4.5 to 2.5 mΩcm at 1000 ℃. However, at a HTT of 2600 ℃, it decreases from 1.45 mΩcm to 1.23 mΩcm with the addition of 15% synthetic graphite in the green coke and then remains almost constant at around 1.2 mΩcm on further addition of synthetic graphite in the green coke. Finally, the expected value of thermal conductivity at a HTT of 1000 °C is seen to increase gradually from 29 to 52 W/mK, while at 2600 ℃, it first increases from 89 to 105 W/mK with the addition of 15% synthetic graphite in the green coke and then remains almost constant (105–111 W/mK) with the further addition of synthetic graphite in the green coke, like the electrical resistivity. The gradual decrease in the electrical resistivity and increase in the thermal conductivity with the increase in synthetic graphite content at a HTT of 1000 ℃ is due to significantly higher electrical and thermal conductivity of the synthetic graphite (which is already heat-treated to around 2600 ℃) compared to the carbonised green coke (which is heat-treated to only 1000 ℃). However, at a HTT of 2600 ℃, the variation in the electrical resistivity and also the thermal conductivity with the increasing synthetic graphite content is due to the overall effect of relatively higher electrical and thermal conductivity of the synthetic graphite compared to the graphitised green coke, and the decreasing compactness of the plates (as revealed from their decreasing bulk density as well as bending strength together with increasing porosity) with the increasing synthetic graphite content in the green coke - synthetic graphite mixture.

Regarding the microstructure, Fig. 19 (a, b) reveals the precursor coal tar pitch to be isotropic and the green coke obtained from it to be having large domains of mesophase. On the other hand, all the green coke based composite plates (HTT = 1000 ℃) containing 0, 15, 30 and 45% of synthetic graphite are found to have fine and homogeneous microstructure which can be seen from Fig. (a, b, c, d).

Thus, it is seen that the addition of 15–45% of the synthetic graphite in the precursor coal tar pitch is able to lead to a reasonably dense (BD = 1.80–1.84 g cm^{-3}) and strong (BS = 46–61 MPa) carbon composites having high electrical, and thermal conductivities (ρ = 1.17–1.23 mΩcm ; K = 105–111 W/mK) . However, the validity of these results (of small plates) on isostatically-moulded bigger blocks was also to be seen.

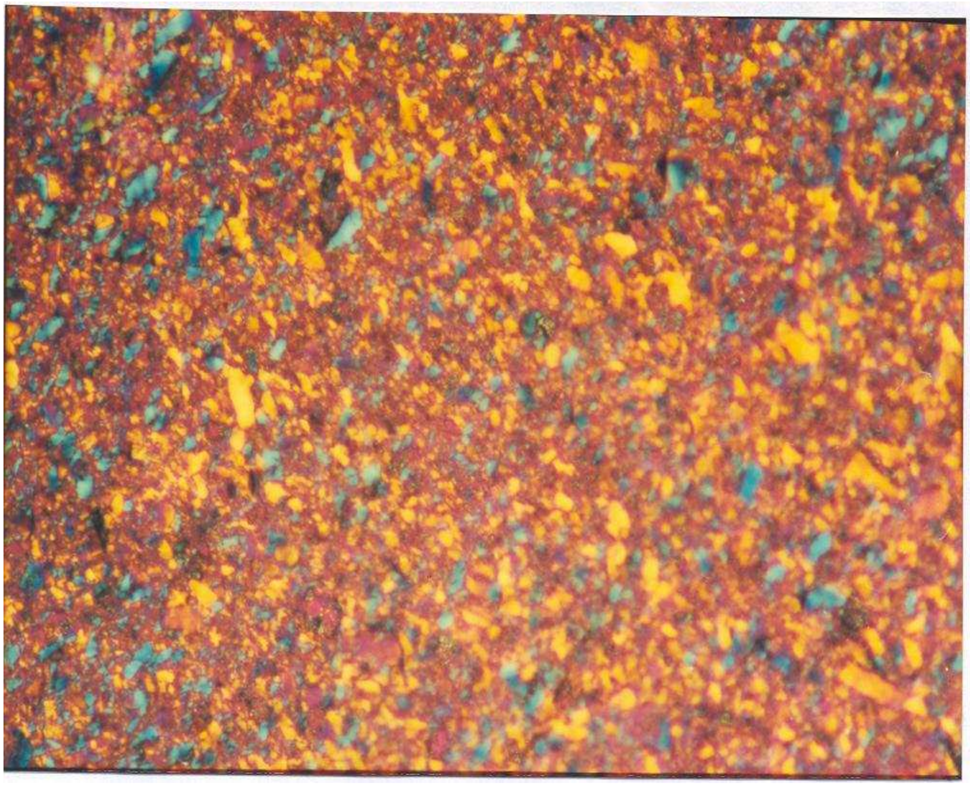


(a)

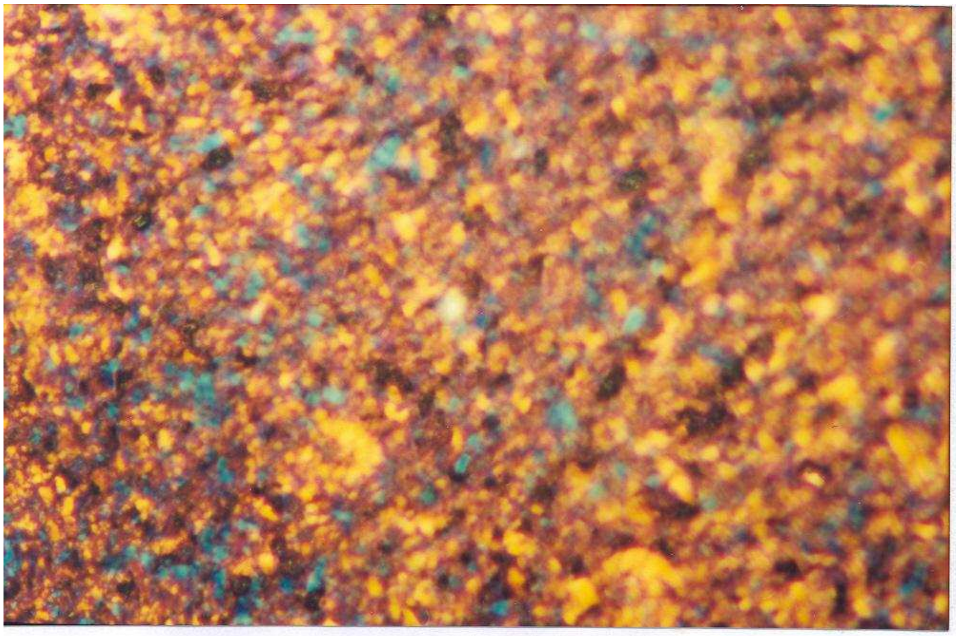


(b)

Fig. 19 (a,b) : Optical micrographs of–(a) precursor coal tar pitch, and (b) resultant green coke (Magnification = 440)

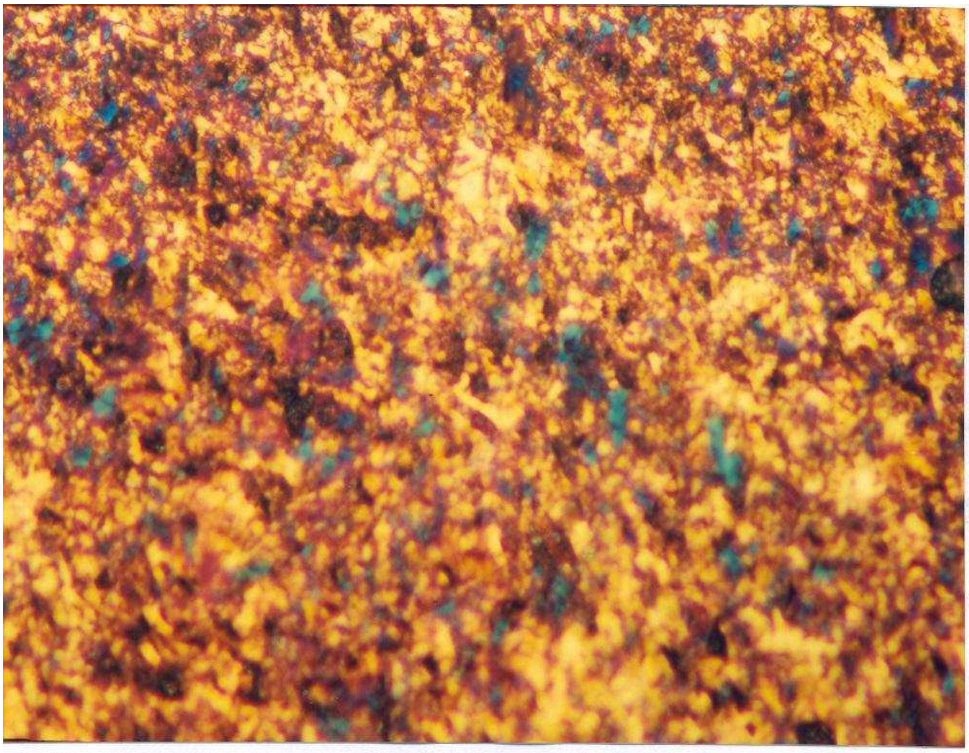


(a)

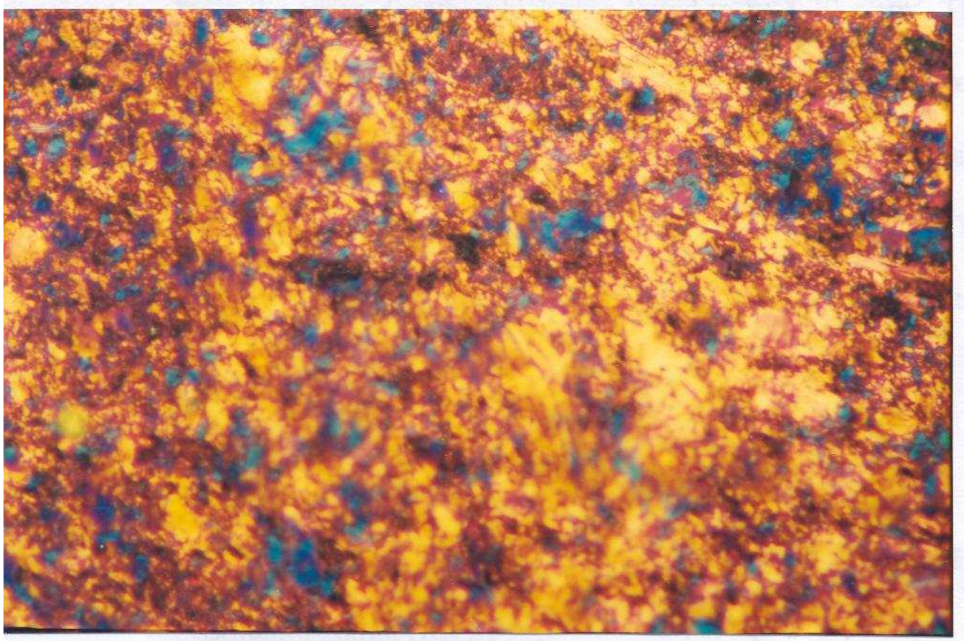


(b)

Fig. 20 (a, b): Optical microstructure of the green coke-based plates incorporating synthetic graphite (2600 °C) (a) 0%, and (b) 15% of synthetic graphite (Magnification = 440)



(c)



(d)

Fig. 21 (c,d) : Optical microstructure of the green coke-based plates incorporating synthetic graphite (2600 ℃) (a) 30%, and (d) 45% of synthetic graphite (Magnification = 440).

6.1 DEVELOPMENT OF CARBON COMPOSITES FROM GREEN COKE INCORPORATING NATURAL GRAPHITE

6.1.1 PURIFICATION OF NATURAL GRAPHITE

A commercial natural graphite (NG) powder was produced and tested for the ash content, which was found to be 11.4%. The ash was characterised w.r.t. spectrochemical analysis, and the NG-powder with respect to sieve-analysis and crystallites parameters, the results of which is given in Table–6. The natural graphite powder was chemically treated to improve its level of purity, and the ash content in the purified NG was reduced to 0.37% as shown in Table–7.

It is observed from Table–6 that the commercial natural graphite has a high ash content of 11.4%, with major impurity components as iron, aluminium, silicon and copper, as revealed from the spectrochemical analysis of the ash.

The X-ray diffraction analysis of this graphite shows the d_{002} and L_C parameters to be 3.358 and 315 A°, respectively. Further, it is seen that the present purification treatment reduces the ash content of the given natural graphite to a value of 0.37% only.

TABLE–6

CHARACTERISTICS OF AS-PROCURED AND PURIFIED NATURAL GRAPHITE

1. Ash in original NG	11.4%
2. Spectrochemical analysis of ash	
Iron	2000 ppm - > 1%
Aluminium	2000 ppm - > 1%
Silicon	1000 ppm - 1%
Copper	1000 ppm - 1%
Calcium	200–2000 ppm
Magnesium	100–1000 ppm
3. Crystallites parameters of purified NG	
d_{002}	3.358 A°
L_C	315 A°
4. Ash in purified NG	0.37%
5. Sieve analysis of purified NG	
-200 + 300 BS mesh (75-50µm)	9 %
- 300 BS mesh (<50 µm)	91 %

6.1.2 DEVELOPMENT OF CARBON COMPOSITES INVOLVING PURIFIED NATURAL GRAPHITE

A coal tar pitch of characteristics shown in Table– 7 was heat-treated at 520 ℃ for 45 minutes in the presence of 0, 15, 30 and 45 % of finely-ground and purified natural graphite (Ash = 0.37 %) to obtain particulate composite, which were ball-milled to fine powders in a centrifugal ball-mill and then solvent-extracted to obtain their modified powders. All these batches of carbon composite powders were pressed into rectangular plates of size 60 mm x 20 mm x 4 mm using a conventional moulding press, and the plates obtained were carbonised to 1000 ℃ and then graphitised to 2600 ℃ in an inert atmosp here. The characteristics of the resulting carbon composite plates at both carbonised as well as graphitised levels [48] are shown in Table–8.

TABLE–7

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH AND THE RESULTING GREEN COKE

S. No.	CHRACTERISTICS	PRECURSOR COAL TAR PITCH	GREEN COKE
1.	Softening point (℃)	90.1	–
2.	Specific gravity	1.27	–
3.	Quinoline insoluble content (%)	0.4	96.3
4.	Toluene insoluble content (%)	19.4	98.4
5.	Coking yield (%)	47.8	91.1

It is seen from Table–8 that the introduction of natural graphite (up to 45%) increases gradually the green density of the composite plates from 1.30 to 1.55 g cm^{-3}. This increase of green density with the increase in the content of natural graphite is due to higher density of the natural graphite compared to the green coke in the green coke - natural graphite mixture. It is further observed from this table that as the natural graphite content in the green coke-natural graphite composite increases from 0 to45%, the weight loss decreases continuously from 7.5% to 5.0 % at 1000 ℃ and 10.1 to 7.5 % at 2800 ℃. This is because of the decreasing content of green coke with the increasing content of the natural graphite in the green coke – natural graphite composites, as it is only the green coke part of the composites which is undergoing weight loss in the form of volatiles, the natural graphite being already heat-treated to around 2800 ℃ will have no weight loss upon heating up to 2600 ℃. The volume and linear

TABLE–8

SUMMARY OF THE CHARACTERISTICS OF GREEN COKE BASED COMPOSITE PLATES (HTT = 1000 / 2800 ℃) HAVING 0–45% OF NATURAL GRAPHITE BY WEIGHT OF PITCH

S. No.	CHARACTERISTICS	VALUES AT NATURAL GRAPHITE PERCENTAGE (BY WEIGHT OF PRECURSOR COAL TAR PITCH) OF			
		0	15	30	45
1.	Green density (g cm^{-3})	1.30	1.49	1.50	1.55
2.	Weight loss (%)	7.5 (10.1)	7.0 (8.8)	5.1 (6.8)	5.0 (7.5)
3.	Volume shrinkage (%)	28.7 (38.8)	20.4 (27.9)	18.7 (24.7)	15.6 (20.7)
4.	Linear shrinkage (%)	10.5 (13.3)	7.1 (8.6)	5.9 (7.0)	5.0 (5.7)
5.	Density amplification factor	1.297 (1.752)	1.168 (1.265)	1.167 (1.238)	1.122 (1.166)
6.	Baked density (g cm^{-3})	1.69 (1.94)	1.73 (1.88)	1.75 (1.90)	1.74 (1.83)
7.	Kerosene density (g cm^{-3})	— (2.24)	— (2.20)	— (2.19)	— (2.18)
8.	Open porosity (%)	— (13.4)	— (14.1)	— (14.6)	— (16.8)
9.	Bending strength (MPa)	76 (63)	60 (47)	46 (41)	37 (31)
10.	Young's modulus (GPa)	15.6 (9.5)	12.5 (9.3)	9.2 (8.7)	8.2 (7.1)
11.	Shore hardness	92 (65)	91 (60)	74 (53)	61 (50)
12.	Electrical resistivity (mΩcm)	4.7 (1.14)	2.4 (0.92)	2.0 (0.85)	1.9 (0.83)
13.	Thermal conductivity* (W/mK)	28 (114)	54 (141)	65 (152)	68 (156)
14.	Ash content (%)	0.50 (0.03)	0.30 (0.04)	0.46 (0.05)	0.46 (0.06)

NOTE : 1. The figures in parentheses refer to the values at a HTT of 2800 ℃.
2. '*' refers to estimated values.

shrinkages, in turn, are observed to decrease continuously from 28.7% to 15.6% and 10.5% to 5.0 % respectively, at a HTT of 1000 ℃ and from 38.8% to 20.7% and 13.3% to 5.7% respectively, at 2600 ℃ , as the natural graphite content in the green coke - natural graphite composites increased from 0 to 45%. This again is due to the fact that it is basically the green coke part of the green coke - natural graphite composite which undergoes shrinkage, as the natural graphite (having no volatile matter) part will have no shrinkage upon this heat treatment.

The overall or resultant effect of the weight loss and the volume shrinkages as a result of heat treatment has been termed as the 'DAF' Accordingly, we can see that the DAF goes on decreasing from 1.297 to 1.222 at 1000 ℃ and from 1.752 to 1.166 at 2600 ℃ as the natural graphite content is increased from 0 to 45%. The net result is that in spite of the gradual increase in the green density as the natural graphite content increases from 0 to 45 %, we have a nominal increase in the value of the bulk density from 1.69 to 1.75 g cm^{-3} at a HTT of 1000 ℃ along with decreasing value from 1.94 to 1.83 g cm^{-3} at a HTT of 2600 ℃ because of the decreasing value of the DA F.

Furthermore, it is seen from Table– that kerosene density of the plates at HTT of 2800 ℃, is higher than the bulk density at this temperature which implies that there is some amount of porosity in the composite plates of all the batches. Accordingly, we see that the open porosity of all GC–NG composites samples goes on increasing with the increase in the natural graphite, attaining values of 13.4–16.8% at 2800 ℃. The bending strength goes on decreasing from an initial value of 76 MPa to a value of 37 MPa at 1000 ℃ and from 63 MPa to 31 MPa at 2800 ℃, with the increasing content of natural graphite from 0 to 45%. The same reasons as mentioned in the case of GC-SG based composite plates explain also the decrease in the bending strength of the plates at both the HTTs of 1000 ℃ as well as 2800 ℃, with the increase in the NG-content in the GC-NG mixture, besides explaining the decrease in the bending strength of the plates on heat-treatment to 2800 ℃ compared to that at the 1000 ℃ . In addition to this, the lowering of the bending strength with the addition of natural graphite is also due to poor wetting of the natural graphite by the binding components of the pitch.

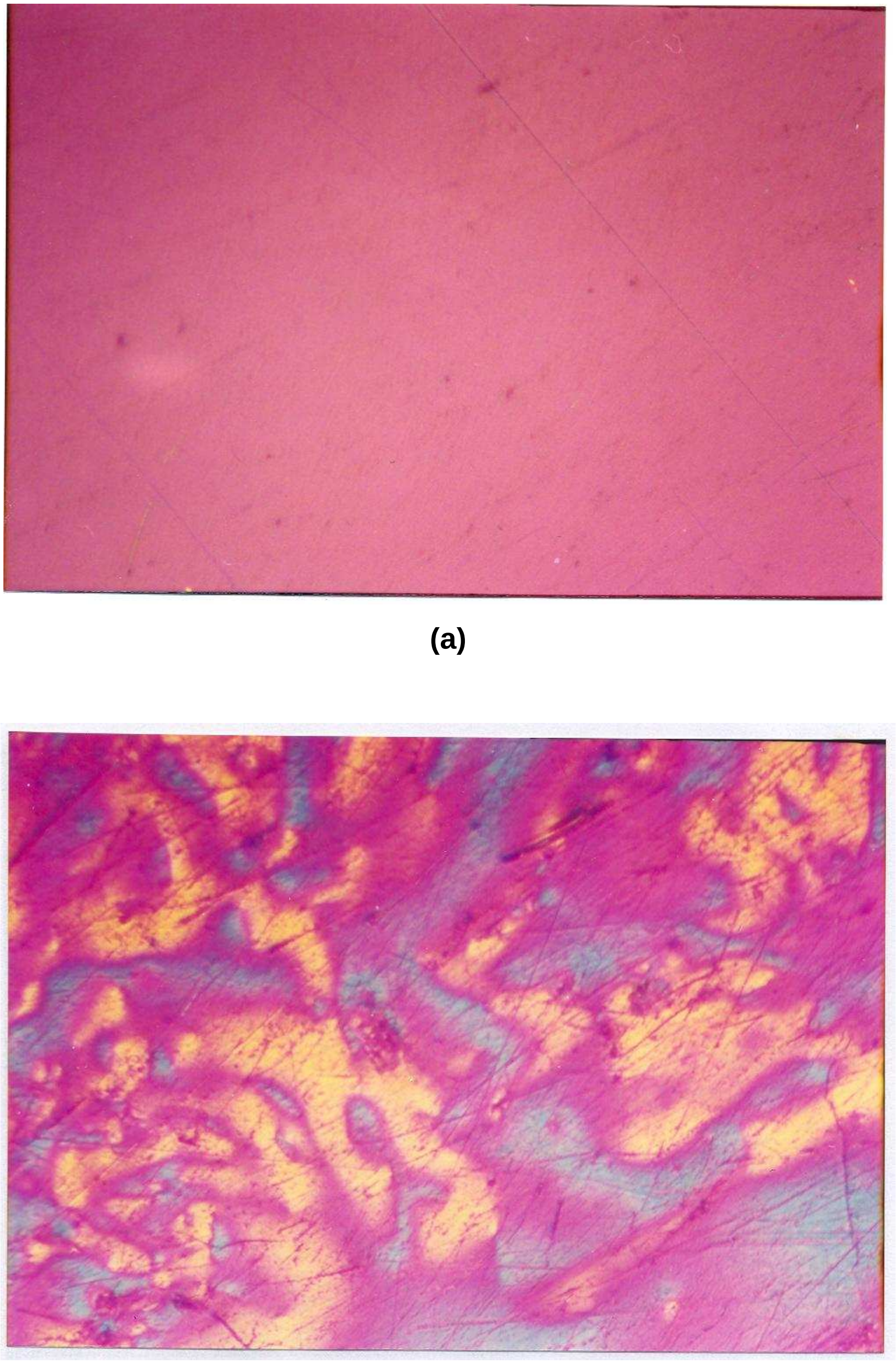
The Young's modulus is seen to decrease from 15.6 to 8.2 GPa at 1000 ℃ and from 9.5 to 7.1 GPa at 2600 ℃, whereas the shore hardness varies in the range of 92–61 at 1000 ℃ and 65–50 at 2800 ℃, whereas the Shore hardness varies in the range of 92–61 at 1000 ℃ and 65–50 at 2800 ℃. Here also, the same reasons as mentioned in the case of GC–SG based composite plates explain the variations of Young's modulus and Shore hardness at both the HTTs of 1000 ℃ and 2800 ℃, as well as their variations with the increase in the NG content.

It is further seen from this table that the electrical resistivity of the composite plates decreases from 4.7 to 1.9 mΩcm at 1000 ℃ and 1.04 to 0.83 mΩcm at 2600 ℃ with the increase in the content of the natural graphite. As a result of this, the estimated value of thermal conductivity goes on increasing from an initial value of 28 W/mK to a value of 68 W/mK at HTT of 1000 ℃, while at 2800 ℃, it first sharply increases from 125 to 152 with the addition of 30% natural graphite in the green coke and then show a slow increase (152–156 W/mK), on further addition of natural graphite in the composite. This continuous decrease in the electrical resistivity or continuous increase in the estimated thermal conductivity with the increase in the natural graphite content at both the HTTs is due to the higher electrical and thermal conductivity of natural graphite compared to that of the carbonised (HTT = 1000 ℃) or graphitised (HTT = 2800 ℃) green coke.

The ash content is found to be (0.30–0.50) % at 1000 °C, which gets greatly reduced to a value in the range of (0.03–0.06)% on graphitisation to 2800 ℃ due to volatilization of most of the impurities at this high temperature of 2800 ℃.

Regarding the microstructure, Fig. 22 (a, b) reveals the precursor coal tar pitch to be isotropic and the green coke obtained from it to be having large domains of mesophase. All the green coke based composite plates (HTT = 2800 ℃) containing 0, 15, 30 and 45% of the natural graphite are found to have fine and homogeneous microstructure which can be seen from Fig. 23-24 (a–d).

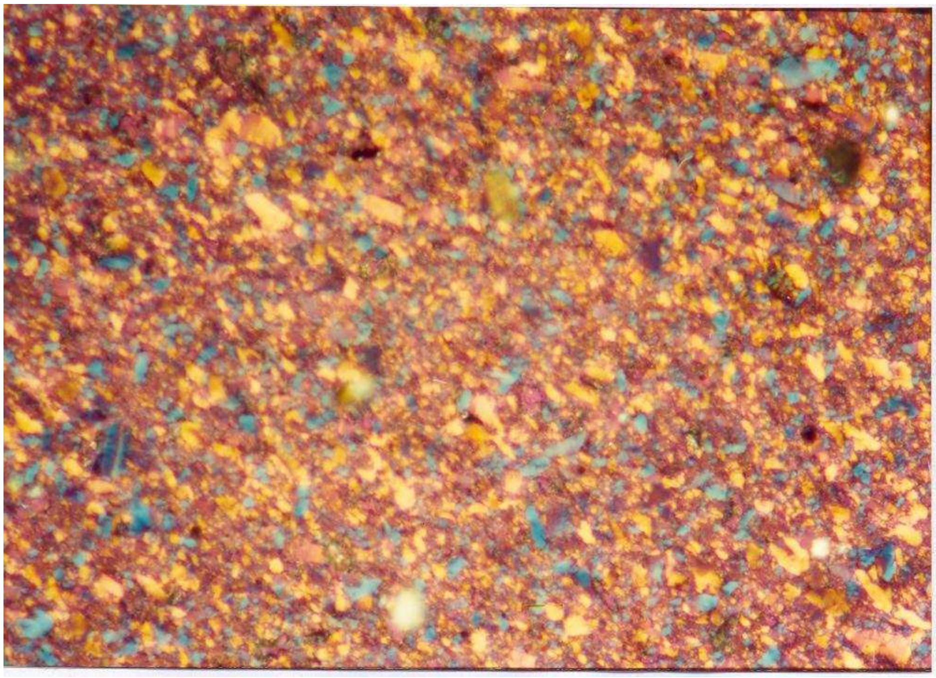
Thus, it can be concluded from this series, that green coke based composite containing 15 to 30% of natural graphite leads to a carbon composite with higher improvement in the electrical and thermal conductivities, compared to the synthetic graphite.



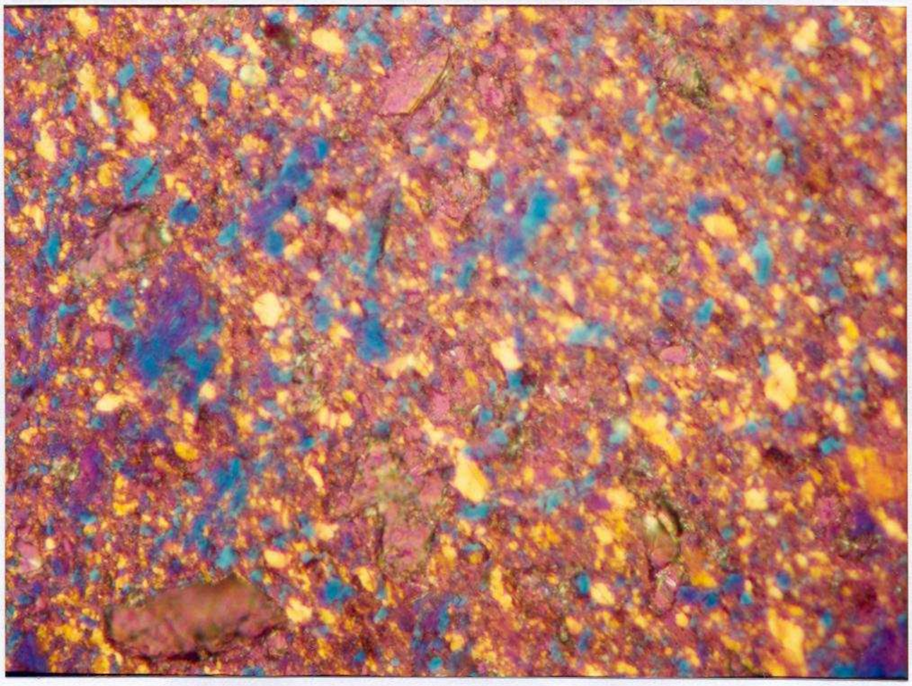
(a)

(b)

<u>Fig. 22 (a, b)</u> : Optical micrographs of – (a) precursor coal tar pitch and (b) resultant green coke (Magnification = 440).

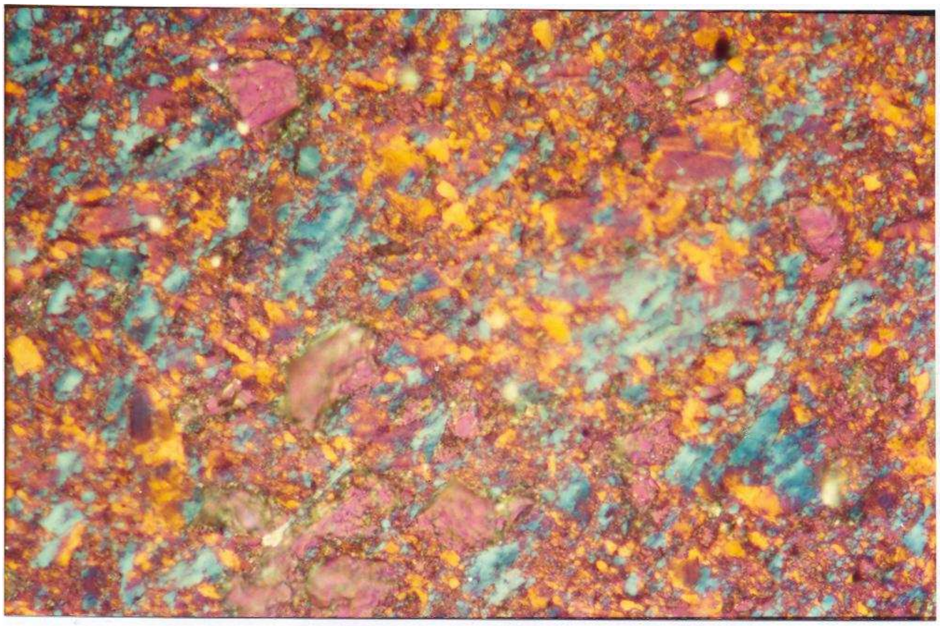


(a)

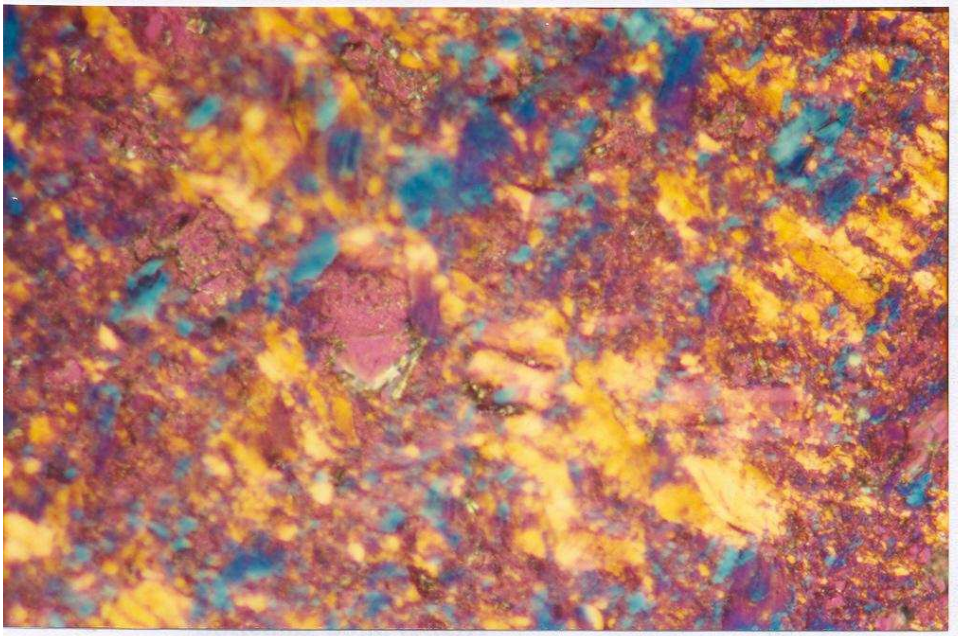


(b)

Fig. 23 (a, b) : **Optical micrographs of green coke-based composite plates (HTT = 2800 °C) containing (a) 0% and (b) 1 5% of natural graphite (Magnification = 440).**



(c)



(d)

Fig. 24 (c, d) : Optical micrographs of green coke-based composite plates (HTT = 2800 ℃) containing (a) 30% and (b) 45% of natural graphite (Magnification = 440).

6.2 DEVELOPMENT OF ISOSTATICALLY - MOULDED CARBON COMPOSITTES FROM GREEN COKE INCORPORATING SYNTHETIC GRAPHITE

From the above-mentioned studies made on the green coke - based carbon composite plates, incorporating, synthetic graphite or purified natural graphite. It was felt to incorporate only some amounts of the synthetic graphite or natural graphite in the green coke and do the isostatic moulding to obtain the cylindrical carbon composite blocks. The study involving addition of synthetic graphite is described and discussed in this section.

Accordingly, four batches of isostatically-moulded carbon composites blocks of graphite were made incorporating 0, 11, 22 and 43 % (by weight of green coke) of finely-ground (mean particle size = 5.5 µm) synthetic graphite. For this purpose, a coal tar pitch was heat-treated at 520 ℃ for 35 min. to obtain the green coke (Table-9), which was ball-milled to a fine powder (mean particle size = 6.5 µm) in a centrifugal ball-mill. The resulting powder was then subjected to solvent extraction in the presence of requisite amounts of the synthetic graphite powder to obtain different composite batches of green cokes and synthetic graphite. These were taken in a rubber mould and pressed isostatically under a pressure of 200 MPa to obtain cylindrical blocks of diameter around 45 mm. The composite blocks were measured for mass and dimensions to obtain the green density and then carbonised to 1000 ℃ and finally graphitised to 2600 ℃ in an inert atmosphere. The carbonised / graphitised composite blocks were finally characterised w.r.t. a number of properties, the values of which are summarised in Table–10. Besides this, the samples of 2600 ℃ heat-treated blocks were subjected to optical microscopy for microstructure examination and the micrographs obtained are shown in Fig. 25-26 (a–d). It is seen from Table–10 that the introduction of synthetic graphite up to 43 % (by weight of green coke) increases gradually the green density of the composite blocks from 1.31 to 1.43 g/cm^3. This is quite obvious as the synthetic graphite, which is already heat-treated to around 2600 ℃, is denser than the green coke which is heat-treated to only 520 ℃. Further, the weight loss is seen to decrease continuously with the increase in the content of SG in the GC–SG mixtures from 12.2 to 8.2 % at a HTT of 1000 ℃

TABLE–9

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH AND THE RESULTING GREEN COKE

S. No.	CHRACTERISTICS	PRECURSOR COAL TAR PITCH	GREEN COKE
1.	Softening point (℃)	101	–
2.	Specific gravity	1.29	–
3.	Quinoline insoluble content (%)	0.0	95.9
4.	Toluene insoluble content (%)	9.5	96.7
5.	Coking yield (%)	45.6	90.1

and 14.2 to 9.6 % at 2600 ℃. As has been said earlier also, this is because of the decreasing content of the green coke (in the composites) which alone is undergoing weight loss in the form of volatiles, the synthetic graphite, being already heat-treated to 2600 ℃, will have no weight loss up to this temperature.

The volume shrinkage, being associated with the weight loss, is seen to follow the same trend as the weight loss and decreases continuously from 31.9 to 23.7 % and 40.3 to 26.3 % at HTTs of 1000 ℃ and 2600 ℃, respectively, with the increase in the synthetic graphite content in the GC–SG composites. Again, this continuous decrease in the volume shrinkage is due to the fact that it is basically the green coke part of the GC–SG composite which actually is undergoing shrinkage and not the synthetic graphite (which is already heat-treated to around 2600 ℃).

TABLE–10

CHARACTERISTICS OF ISOSTATICALLY-PRESSED CARBON COMPOSITES BLOCKS (1000 / 2600 ℃) HAVING DIFFERENT RATIOS OF GREEN COKE (GC) AND SYNTHETIC GRAPHITE (SG)

S. No.	CHARACTERISTICS	VALUES AT SYNTHETIC GRAPHITE PERCENTAGE (BY WEIGHT OF GREEN COKE)			
		0	11	21	43
1.	Green density (g cm^{-3})	1.31	1.38	1.42	1.43
2.	Weight loss (%)	12.2 (14.2)	11.5 (13.9)	8.7 (10.5)	8.2 (9.6)
3.	Volume shrinkage (%)	31.9 (40.3)	31.7 (35.6)	27.6 (33.9)	23.7 (26.3)
4.	Density amplification factor	1.29 (1.44)	1.29 (1.34)	1.26 (1.35)	1.20 (1.26)
5.	Bulk density (g cm^{-3})	1.69 (1.94)	1.78 (1.93)	1.79 (1.91)	1.72 (1.80)
6.	Kerosene density (g cm^{-3})	— (2.18)	— (2.19)	— (2.19)	— (2.20)
7.	Open porosity (%)	— (11.0)	— (11.9)	— (12.8)	— (18.2)
8.	Bending strength (MPa)	79 (68)	78 (66)	73 (60)	66 (54)
9.	Young’s modulus (GPa)	15.5 (8.9)	14.4 (8.5)	13.7 (8.3)	13.7 (8.0)
10.	Shore hardness	94 (71)	88 (68)	87 (60)	84 (48)
11.	Electrical resistivity (mΩcm)	5.8 (1.86)	4.8 (1.82)	3.9 (1.81)	3.5 (1.80)
12.	Thermal conductivity* (W/mK)	22 (70)	27 (71)	33 (72)	37 (72)
13.	Ash content (%)	— (0.0)	— (0.0)	— (0.0)	— (0.05)

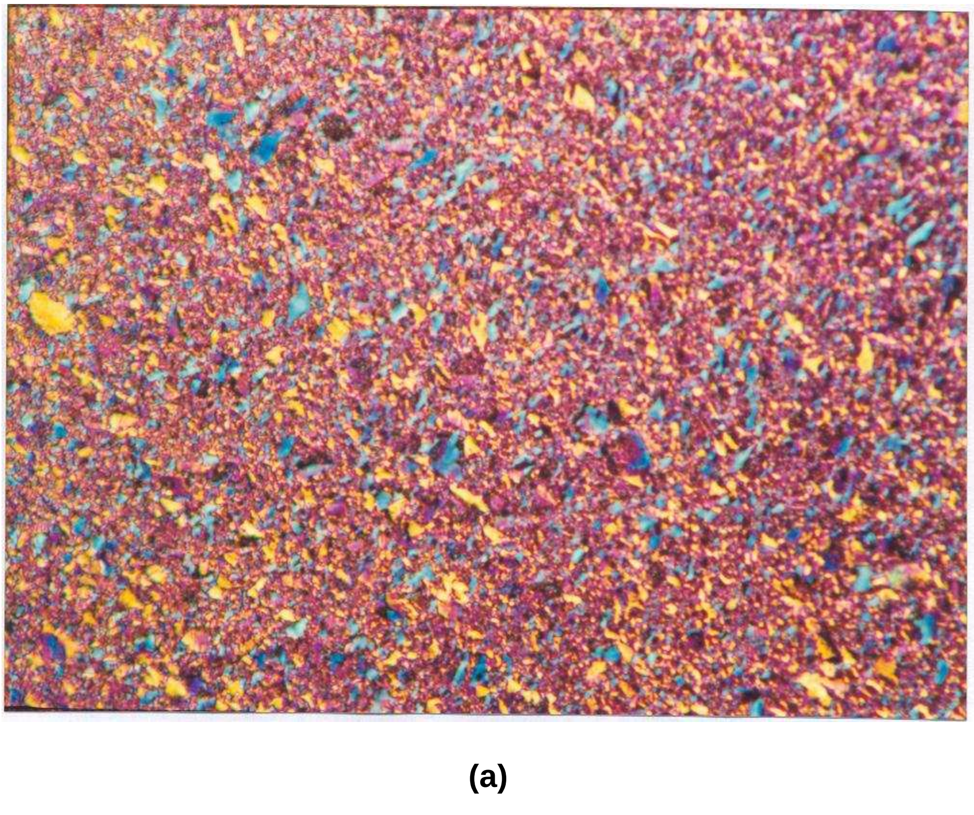
NOTE : 1. The figures in parentheses refer to the values at a HTT of 2600 ℃.
2. ‘*’ refers to estimated values.

The overall or resultant effect of the weight loss and the volume shrinkage as a result of the heat-treatment has been defined by the term, 'Density Amplification Factor (DAF)', which is the ratio of fractional residual weight to the fractional residual volume of the monolithic blocks upon the heat-treatment. We see that the DAF of the carbon composites blocks goes on decreasing with the increase in the content of SG from the initial value of 1.29 to a value of 1.20 at 1000 ℃ and from 1.44 to 1.26 at a HTT of 2600 ℃, respectively. The net result is that at a HTT of 1000 ℃, we have a increasing value of the bulk density from 1.69 to 1.79 g cm^{-3} up to a SG content of 21 %, above which it decreases to 1.72 g cm^{-3} for 43 % of SG content, and a decreasing value of the bulk density (1.94 to 1.80 g cm^{-3}) at a HTT of 2600 ℃. Further, the open porosity of the graphitised composite blocks is seen to increase slowly from 11.0 to 12.8 % with the increase in the content of SG up to a level of 21 % (by weight of GC) in the GC–SG mixture, above which it increases sharply to a value of 18.2 % at 43 % of SG (by weight of the green coke). This may be basically due to decreasing (inadequate) amount of binding components in the GC–SG mixtures.

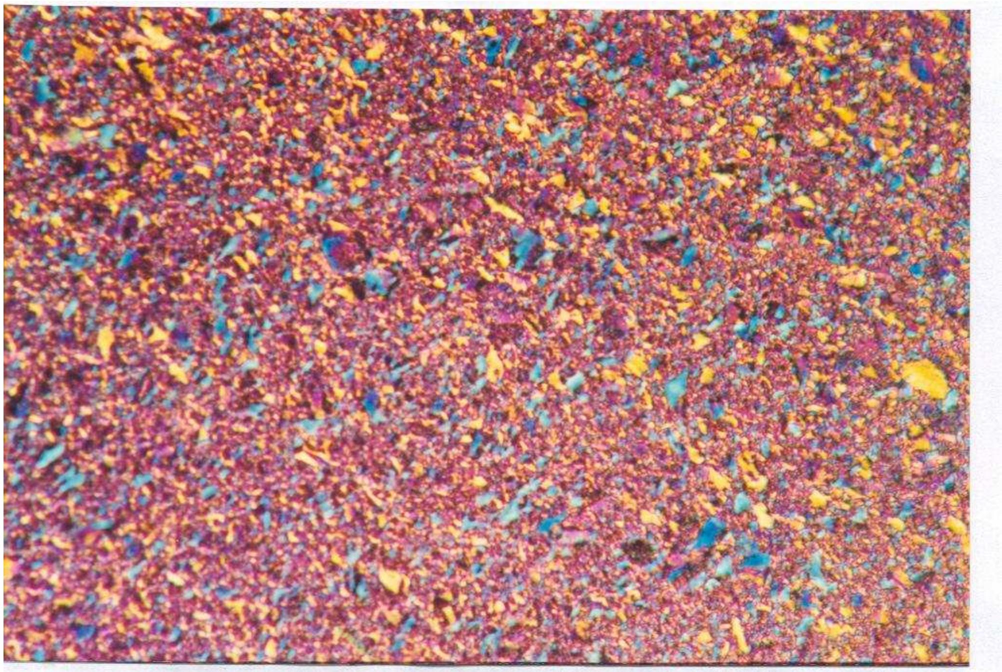
Regarding the bending strength, it is seen that it goes on decreasing with the increasing content of synthetic graphite in the green coke - synthetic graphite mixtures at both the HTTs of 1000 ℃ as well as 2600 ℃ . It thus varies from 79 to 66 MPa at a HTT of 1000 ℃ and from 68 to 54 MPa at 2600 ℃. This may be predominantly due to the decreasing binding components in the GC–SG composite with the increase of SG content. The Young's modulus is seen to decrease from 15.5 to 13.7 GPa at 1000 ℃, and from 8 .9 to 8.0 GPa at 2600 ℃, while the Shore hardness decreases continuously from 94 to 84 at 1000 ℃ and from 71 to 48 at a HTT of 2600 ℃. The reasons for these variations of Young's modulus and Shore hardness w.r.t. HTT as well as SG content have already been discussed in earlier sections.

Further, it is also seen from the Table–10 that the electrical resistivity of the isostatically - moulded composite blocks gradually decreases from 5.8 to 3.5 mΩcm at 1000 ℃ as SG content is increased. However, at 2600 ℃, it is found to be nominally decreasing from 1.86 to 1.80 mΩcm, with the increase in the synthetic graphite content. Here again, it may be noted that the value of electrical resistivity of isostatically - moulded composite blocks containing SG is found to be somewhat higher than that of the corresponding unidirectionally-moulded composite plates (results of which are discussed in the earlier sections). Regarding the expected value of thermal conductivity at a HTT of 1000 °C, it is seen to increase gradually from 22 to 37 W/mK, while at 2600 °C, it shows almost no increase (from 70 to just 72 W/mK only) with the increase of synthetic graphite in the composites from 0 to 43 % (by weight of green coke). Further, the ash content of the carbon composite blocks is found to be negligible (0–0.05 %). Finally, it can be seen from Figs.25-26 (a–d) that all the green coke based graphites modified by incorporating the synthetic graphite have a fine and homogenous microstructure.

Thus, it may be noted from the results of this series of experiments that although the addition of synthetic graphite (up to 43 %) does not cause substantial fall in the bending strength, it does also not increase the thermal conductivity of the blocks, though all the other characteristics of this special graphite are achieved.

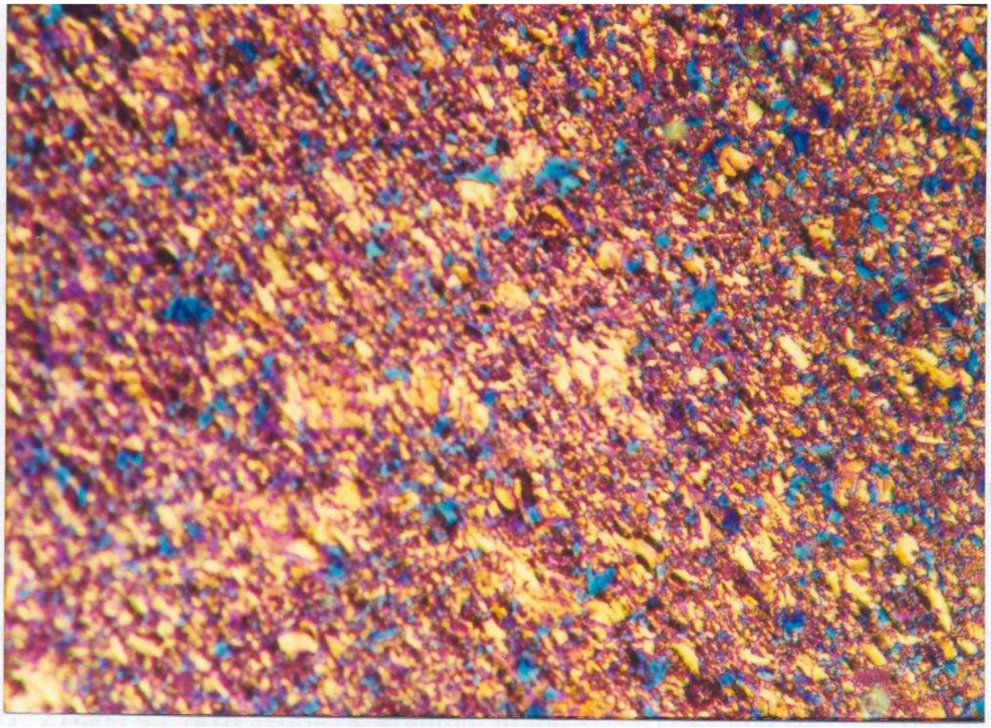


(a)

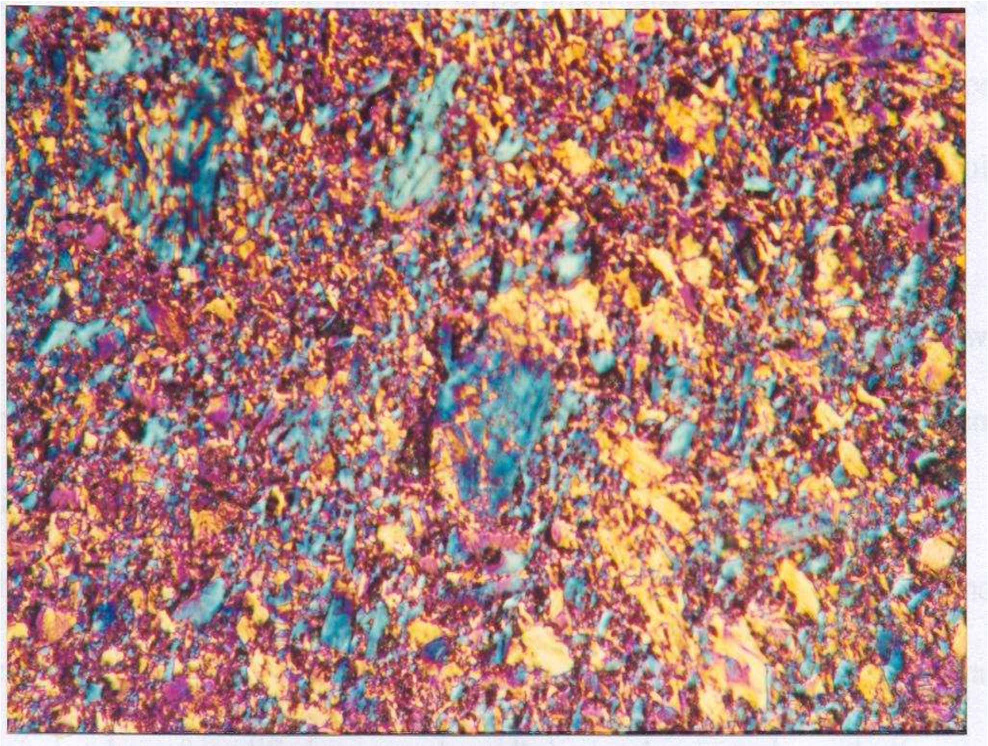


(b)

Fig.25 (a,b) : Optical micrograph of isostatically-moulded green coke-based graphite (HTT = 2600 °C) containing (a) 0 % , and (b) 11 % of synthetic graphite (by weight of green coke) (Magnification = 440).



(c)



(d)

Fig.26 (c,d): **Optical micrograph of isostatically-moulded green coke-based graphite (HTT = 2600 °C) containing (c) 21 % , and (d) 43 % of synthetic graphite (by weight of green coke) (Magnification = 440).**

6.3 DEVELOPMENT OF ISOSTATICALLY-MOULDED CARBON COMPOSITES FROM GREEN COKE INCORPORATING NATURAL GRAPHITE

It was, also, decided to incorporate only the natural graphite in the green coke in order to modify the carbon composites for achieving the required value of thermal conductivity of the resultant composite block.

Accordingly, four batches of isostatically-moulded carbon composite blocks were made incorporating 0, 16, 21 and 43 % (by weight of green coke) of finely-ground natural graphite in the green coke. As usual, a coal tar pitch with suitable properties, as shown in Table–11, was heat-treated to obtain a green coke, which was ball-milled and solvent-extracted in the presence of requisite amounts (by weight) of finely-ground natural graphite to obtain batches of modified green coke. All the batches were isostatically-moulded into carbon composite blocks, which were then carbonised to 1000 ℃ and finally graphitised to 2600 ℃ in the usual manner. The isostatically-moulded composite blocks were characterised at both carbonised and graphitised levels and the values obtained are summarised in Table–12. The microstructure of 2600 ℃ heat-treated blocks was also examined on an optical microscope, and the micrograph obtained is shown in Fig.27-28.

TABLE–11

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH AND THE RESULTING GREEN COKE

S. No.	CHRACTERISTICS	PRECURSOR COAL TAR PITCH	GREEN COKE
1.	Softening point (℃)	98	–
2.	Specific gravity	1.28	–
3.	Quinoline insoluble content (%)	0.0	96.6
4.	Toluene insoluble content (%)	10.5	97.7
5.	Coking yield (%)	46.4	91.1

It is seen from Table–12 that the addition of natural graphite up to 43 % increases continuously the green density of the composite blocks from 1.31 to 1.51 g/cm^3. This is due to higher density of the natural graphite (which is free from any volatile matter) compared to green coke, which is heat-treated to only 520 ℃ and contains some volatile matter.

The weight loss of the green carbon composite blocks on carbonisation is seen to decrease continuously with the increase in the content of natural graphite (NG) in the GC–NG mixtures from a value of 11.2 to 6.1% at a HTT of 1000 ℃ and from 14.2 to 7.3 % at a HTT of 2600 ℃. As explained earlier also, this is because of the fact that it is only the green coke which alone is undergoing weight loss in the form of volatiles, while the natural graphite being free from volatile matter will have no weight loss up to 2600 ℃.

TABLE–12

CHARACTERISTICS OF ISOSTATICALLY-PRESSED CARBON COMPOSITES (HTT = 1000 / 2600 °C) HAVING DIFFERENT RATIOS OF GREEN COKE (GC) AND NATURAL GRAPHITE (NG)

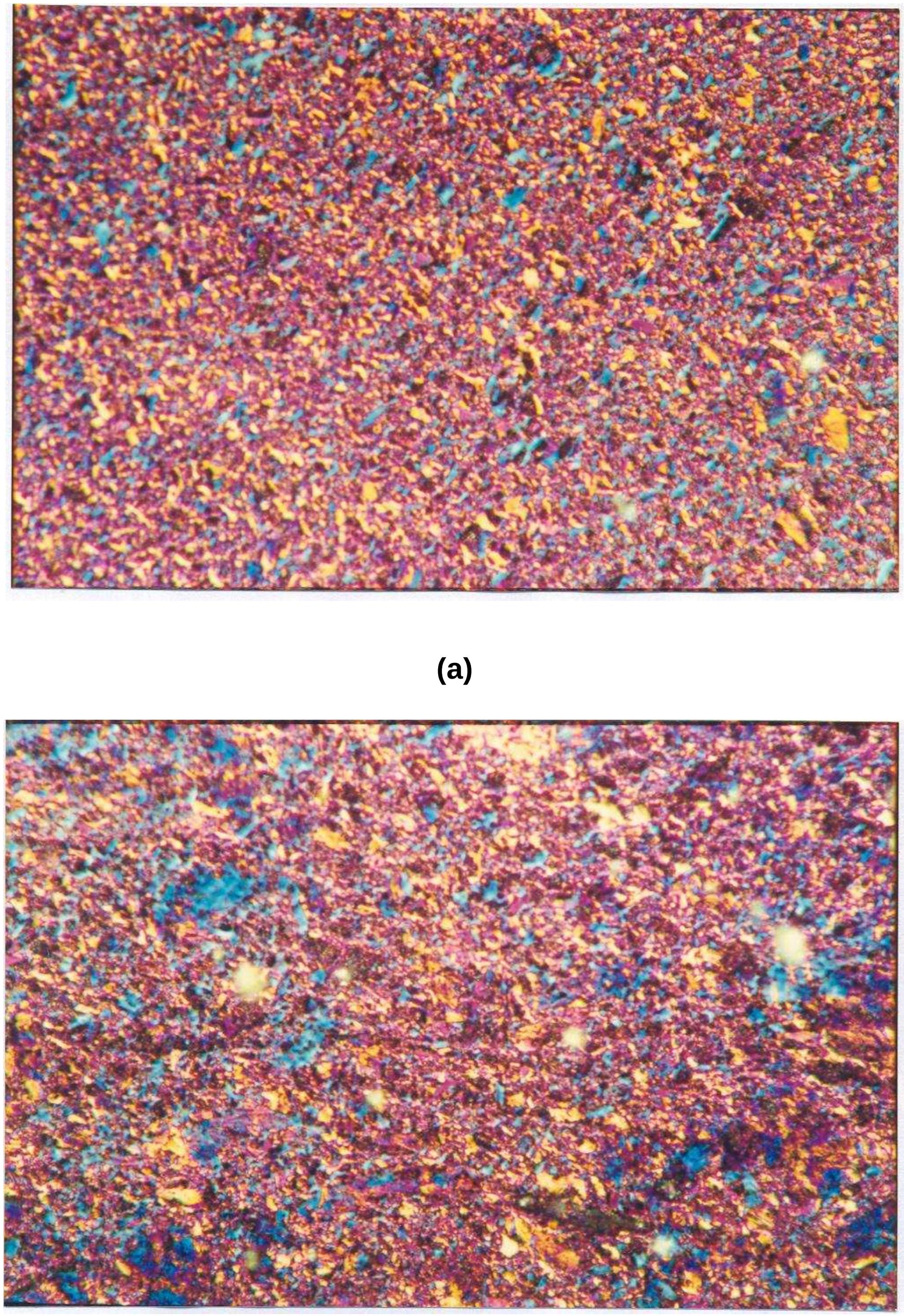
S. No.	CHARACTERISTICS	VALUES AT NATURAL GRAPHITE PERCENTAGE (BY WEIGHT OF GREEN COKE)			
		0	16	21	43
1.	Green density (g cm^{-3})	1.31	1.41	1.44	1.51
2.	Weight loss (%)	11.2 (14.2)	10.0 (12.4)	7.7 (9.1)	6.1 (7.3)
3.	Volume shrinkage (%)	30.9 (40.1)	27.5 (31.5)	25.8 (32.3)	21.3 (25.6)
5.	Density amplification factor	1.29 (1.44)	1.24 (1.35)	1.24 (1.34)	1.19 (1.25)
6.	Bulk density (g cm^{-3})	1.69 (1.89)	1.75 (1.90)	1.79 (1.94)	1.80 (1.91)
7.	Kerosene density (g cm^{-3})	— (2.18)	— (2.20)	— (2.21)	— (2.23)
8.	Open porosity (%)	— (13.3)	— (13.6)	— (12.2)	— (14.3)
9.	Bending strength (MPa)	79 (68)	65 (52)	55 (45)	46 (40)
10.	Young's modulus (GPa)	15.5 (8.9)	14.8 (8.7)	13.9 (8.5)	13.3 (8.2)
11.	Shore hardness	94 (71)	69 (59)	62 (49)	59 (46)
12.	Electrical resistivity (mΩcm)	5.6 (1.84)	3.9 (1.40)	3.2 (1.23)	3.0 (1.22)
13.	Thermal conductivity* (W/mK)	23 (70)	33 (93)	41 (105)	43 (106)
14.	Ash content (%)	— (0.0)	— (0.03)	— (0.05)	— (0.09)
15.	Thermal expansion (10^{-6} /K)	— (5.2)	— (5.5)	— —	— —

NOTE : 1. The figures in parentheses refer to the values at a HTT of 2600 °C.
2. '*' refers to estimated values.

Similarly, the volume shrinkage decreases from an initial value of 30.9 % at 1000 ℃ and 40.1 % at 2600 ℃ at 0 % addition of NG to a final value of 21.3% at 1000 ℃ and 25.6% at 2600 ℃ on addition of 43 % NG in the green coke. This again is because of the fact that it is only the green coke part of the GC–NG composites which actually is undergoing the shrinkage.

Further, it was observed that the DAF goes on decreasing with the increase in NG content in the GC–NG composites from 1.29 to 1.19 at a HTT of 1000 ℃, and from 1.44 to 1.25 at a HTT of 2600 ℃. The net result is that we have a increasing value of the bulk density at a HTT of 1000 ℃ but an almost the same value (1.89 –1.94 g/cm^3) at a HTT of 2600 ℃, because of the decreasing value of DAF (at both the HTTs –1000 as well as 2600 ℃). It is further observed that the kerosene density of the graphitised blocks is higher than the corresponding bulk density at 2600 ℃, thereby showing the presence of open porosity in all the batches.

Furthermore, the bending strength of the composite blocks moulds shows a decrease in the values from 79 to 46 MPa at a HTT of 1000 ℃ and 68 to 40 MPa at HTT of 2600 ℃ for 0 to 43 % addition of natural graphite in the green coke. This decrease may be due to the presence of NG in the GC–NG composites as NG does not bind well due to its crystalline structure. The Young's modulus also decreases from 15.5 to 13.3 GPa and 8.9 to 8.2 GPa at HTTs of 1000 ℃ and 2600 ℃, respectively. The Shore hardness is also seen to decrease from a value of 94 to 59 at 1000 ℃ and from 71 to 46 at 2600 ℃. These variations of the bending strength and Shore hardness with the increase in the heat-treatment temperature for all the GC–NG mixtures based blocks are due to the growth of crystallites at the expense of the disorganised matter cross-linked between them.



(a)

(b)

<u>Fig. 27 (a, b):</u> **Optical micrograph of isostatically-moulded green coke-based carbon composite (HTT = 2600 °C) containing (a) 0 % , and (b) 16 % of natural graphite (by weight of green coke) (Magnification = 440).**

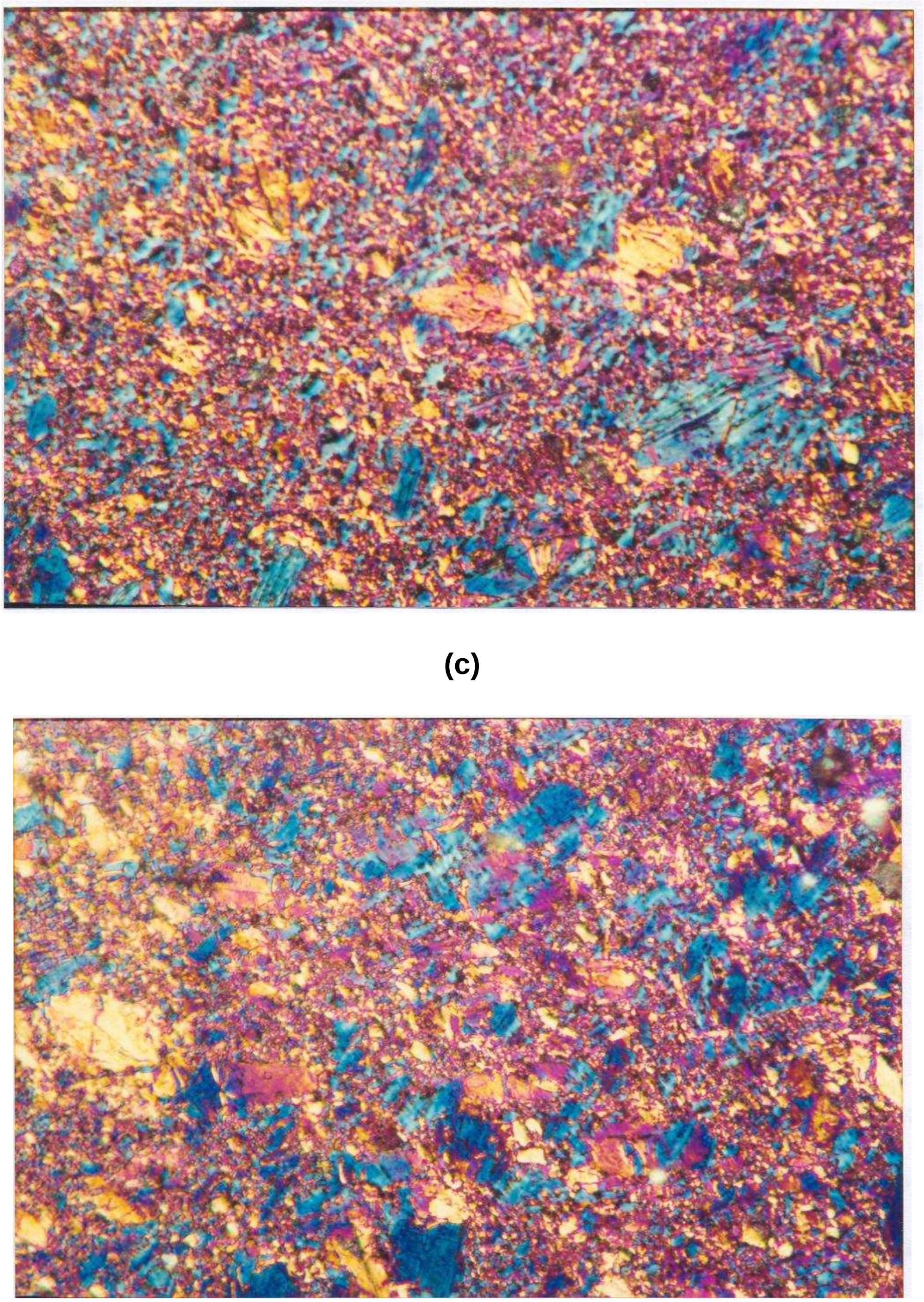


Fig.28(c, d): **Optical micrograph of isostatically-moulded green coke-based carbon composite (HTT = 2600 ℃) containing (c) 21 % , and (d) 43 % of natural graphite (by weight of green coke) (Magnification = 440).**

Regarding the electrical resistivity of the blocks, it can be seen from Table– 12 that it gradually decreases from a value of 5.6 to 3.0 mΩcm at 1000 °C as NG content increases from 0 to 43 % in the GC–NG composite. However, at 2600 °C, it first decreases steeply from 1.84 to 1.40 m Ωcm at 16 % addition of NG in the GC–NG composite, then remains nearly constant, showing a value of 1.22–1.23 mΩcm at (21–43) % addition of NG. The estimated value of thermal conductivity is seen to increase from a value of 22 to 43 W/mK with the increasing content of NG in the GC–NG composite at 1000 C, and from 70 to 106 at 2600 °C. Thus, (16–43) % of NG (by weight of green coke) in the GC–NG mixture is able to lead to a graphite of thermal conductivity of $\geq$ 90 W/mK.

Further, the ash content of the graphitised blocks is observed to be negligible (varying in the range 0–0.09 %) for the different GC–NG composite batches. Furthermore, the values of thermal expansion of the graphite having zero and 16 % of natural graphite (by weight of green coke) are found to be 5.2×10^{-6} and 5.5×10^{-6} / K, respectively. Finally, it can be seen from Figs. 27-28 (a–d) that all the green coke based carbon composites modified by incorporating the natural graphite have a fine and homogeneous microstructure.

It may thus be concluded from this series of experiments that isostatically-moulded green coke carbon composites by the addition of (16–21) % NG (by weight of green coke) meets all the desired specifications.

7.0 FABRICATION OF CARBON-CARBON COMPOSITES

Carbon fibre reinforced carbon composites were made by using the slurry forming technique. First of all the suitable quantity of green coke(~15gm) which is used as matrix material of composites is weighed. Chopped carbon fibres are ground to reduce the size to 6mm and to disperse them from the bundle form. High softening point pitch, which is used binding agent between the green coke and carbon fibres is weighed (.3gm) and dissolved in 40ml of toluene. The solution is heated to completely dissolve the high softening point pitch. When the pitch is completely dissolved add preweighed carbon fibres are added to the solution and stirr it well to have an uniform coating of high softening point pitch over the carbon fibres. After this preweighed green coke is added to the solution of pitch and carbon fibres and stirred to have fine dispersion of carbon fibres into the mixture. The toluene is allowed to evaporate at room temperature. To ensure the complete removal of toluene, the mixture is heated in a oven at around 110^{o}C for about ½ hour. Now, the powdered mixture(3.0gm) is taken to make mold of it. Molding of mixture is done in a chrome-steel die on a typical hydraulic press at a pressure of around 200 MPa. The size of the die is 40x10x5mm. The load is applied for 8 minutes. After 8 minutes the molded product is taken out from the die. The molded article in form of a plate is measured in terms of green density, green length, green breadth, green thickness and green volume.

7.1 CHARACTERISTICS OF CHOPPED MESOPHASE CARBON FIBRES

Tensile strength (TS) = 3.4 GPa

Tensile modulus (TM) = 830 GPa

Elongation = .3%

Density = 2.2 gm/cc

Electrical resistivity (ER) = .21mΩcm

Thermal conductivity (TC) = 540 W/mK

Sizing amount (desized) = .1%

Chopped length = 6 mm

Diameter = 10 µm

Carbon content = 99%

7.2 CHARACTERISTICS OF GREEN COKE

Quinoline insoluble content (QI) = 97.3%

Toluene insoluble content (TI) = 97.9%

Coking value (CV) = 91.7%

7.3 RESULTS AND DISCUSSION

TABLE 13: DENSITY OF C-C C0MPOSITE SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Density (gmcm^{-3}) at heat treatment of			
		RT	1000^{o}C	1400^{o}C	2500 ^{o}C
S1	100:OO	1.31	1.68	1.78	1.85
S2	95:5	1.34	1.58	1.74	1.82
S3	90:10	1.35	1.54	1.68	1.78

The density of composite plates is increasing with the increasing heat treatment. The change in density is due to the high volume shrinkage and low weight loss. The plate S3 with 10% CF show maximum density at room temperature.The density will increase, after the heat treatment. Reason for the least density of S3 sample is high weight loss of green coke coupled with low volume shrinkage because of presence of CF.

TABLE 14: WEIGHT LOSS OF C-C COMPOSITE SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Weight loss (%) at heat treatment of		
		1000^{o}C	1400^{o}C	2500 ^{o}C
S1	100:00	8.9	9.83	18.4
S2	95:5	7.8	9.2	14.4
S3	90:10	6.9	8.10	11.2

In Table-14 weight loss of plates at different heat treatments is given. The weight loss is increased with the increasing heat treatment upto higher temperatures. The weight loss of S1 is greater as compared to S2 and S3. This is because, the weight loss is shown by only green coke.

TABLE 15: VOLUME SHRINKAGE(VS) C-C COMPOSITE OF SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Volume shrinkage (%) at heat treatment of		
		1000°C	1400 °C	2500 °C
S1	100:00	29.3	33.7	41.4
S2	95:0	25.23	29.7	35.2
S3	90:10	23.14	28.2	31.7

Volume shrinkage of composite plates is reported in Table-16, due to presence of carbon fibres, plates with higher percentage of CF s how least volume shrinkage.

TABLE 16: LINEAR SHRINKAGE(LS) C-C COMPOSITE OF SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Linear shrinkage (%) at heat treatment of		
		1000°C	1400 °C	2500 °C
S1	100:00	10.41	11.96	17.32
S2	95:5	7.9	11.6	15.71
S3	90:10	8.9	10.03	12.42

Linear shrinkage of composite plates is because of the presence of green coke not by CF. Plate S1 with no carbon fibre shows maximum linear shrinkage. Plates with CF has less linear shrinkage because fibres used are graphitised and shows no change in its physical properties upon heat treament.

TABLE 17: ELECTRICAL RESISTIVITY (ER) OF COMPOSITE SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Electrical resistivity (mΩcm) at heat treatment of		
		1000°C	1400°C	2500 °C
S1	100:00	3.78	3.16	2.39
S2	95:5	3.23	2.38	1.98
S3	90:10	2.86	2.24	1.67

Electrical resistivity of composite plates decreases with heat treatment to higher temperatures. The decrease in electrical resistivity with HTT is due to the removal of hetero atoms and improvement in size of crystallite. With increasing percentage of carbon fibres electrical resistiviy is decreasing due to the low electrical resitivity of carbon fibres (as reported in characteristics of CF above).

TABLE18: THERMAL CONDUCTIVITY (K) OF COMPOSITE SAMPLES AT DIFFERENT HEAT TREATMENTS

Sample No.	GC:CF	Thermal conductivity (W/mK) at heat treatment of		
		1000°C	1400 °C	2500 °C
S1	100:00	34.286	41.013	54.23
S2	95:5	40.124	54.454	65.45
S3	90:10	45.315	57.857	77.61

Table – 18 summarize the thermal conductivity of composite plates at different heat treatments. As the plates were subjected to higher heat treatment at higher temperatures, thermal conductivity goes on increasing. This is also increasing with increasing fibre content in the plate.

8.0 CONCLUSIONS

1. A suitable self-sintering green coke powder has been developed from a QI-free coal tar pitch (made by our own process) as well as from the commercially available low-QI coal tar pitch by heat-treatment. This has been successfully used to produce a dense, strong and high purity graphite having a homogeneous and fine microstructure.

2. The additions of synthetic graphite (15–45 %) and purified natural graphite (15–30 %) in the precursor pitch to obtain modified green coke is able to lead to a carbon composite (in the form of plates) of desired specifications with improved values of thermal conductivity. These values are (93–100), (105–111) and (141–152) W/mK, respectively, for the green coke based graphite plates modified by the additions of either of, synthetic graphite or natural graphite.
3. The isostatic moulding of a solvent-extracted green coke leads to a high density - high strength – carbon composite blocks of relatively lower electrical resistivity (or correspondingly lower thermal conductivity) compared to that of graphite plates.
4. The modification of green coke by the addition of synthetic graphite (11–43 % by weight of the green coke) does not cause any significant improvement in the thermal conductivity of the resulting isostatically-moulded composite blocks.

5. The modification of green coke by the addition of natural graphite (16– 21 % by weight of the green coke) causes a substantial improvement in the thermal conductivity of the resulting isostatically-moulded composite blocks (K = 105 W/mK).

6. Carbon fibre reinforced carbon composites can be developed from carbon fibres reinforced in the matrix obtained by the use of green coke.
7. It is concluded that using carbon fibres as reinforcements, almost all the properties of composites improved.

9.0 REFERENCES

1. Bragg W.H. and Bragg W.L., Proc. Royal Soc. London, A89 (1913), p. 277.
2. Seal M., Nature, 185 (1960) 522.
3. Hall H.T., Proc. 3rd Carbon Conf. (Pergamon Press, New York, 1959), p. 75.
4. Hull A.W., Phys. Rev., 10 (1917) 661.
5. Bernal J.D., Proc. Royal Soc. London, A106 (1924), p. 749.
6. Lipson H. and Stockes A.R., Proc. Royal Soc. London, A181 (1942), p. 101.
7. Boehm H.P. and Hofmann U., Z. Anorg. Allgemein. Chern., 278 (1955) 58.
8. Boehm H.P. and Coughlin R.W., Carbon, 2 (1964) 1.
9. Basset M.J., J. Phys. Radium 10 (1939) 217.
10. Jones M.T. and Weltner W., Proc. 4th Carbon Conf. (Pergamon Press, New York, 1960), Unpublished.
11. Biorenkerk H.P., Bundy F.P., Hall H.T., Stong H.M. and Wentorf (Jr.) R.H., Nature, 184 (1959) 1094.
12. Bundy F.P., J. Chem. Phys., 38 (1963) 618.
13. Noda T. and Matsuoka H., Proc. Int. Symposium on High Temp. Technol. (McGraw Hill Book Co., New York, 1959), p. 286.
14. Bundy F.P., Bassett W.A., Weathers M.S., Hemley R.J., Mao H.K. and Goncharov A.F., Carbon, 34 (1996) 141.
15. Kroto H.W., Heath J.R., O'Brein S.C., Curl R.F. and Smalley R.E., Nature, 318 (1985) 162.
16. Kratschmer W., Fostiropoulos K. and Huffman D.R., Chem. Phys. Lett., 170 (1990) 167.
17. Kratschmer W., Lamb L.D., Fostiropoulos K. and Huffman D.R., Nature, 347 (1990) 354.
18. Lijima S., Nature, 354 (1991) 56.
19. Dutta A.K., Phys. Rev., 90 (1953) 187.
20. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 86.
21. Text book “ Carbon Fibres” by Bahl O.P., Ross A. Roger, Shen Zengwin and Lavin Gerard J, 1.
22. Text book “ Carbon Fibres” by Bahl O.P., Ross A. Roger, Shen Zengwin and Lavin Gerard J, 2.

23. Text book “ Carbon Fibres” by Bahl O.P., Ross A. Roger, Shen Zengwin and Lavin Gerard J, 31.
24. Text book “ Carbon Fibres” by Bahl O.P., Ross A. Roger, Shen Zengwin and Lavin Gerard J, 41.
25. Text book “ Carbon Fibres” by Bahl O.P., Ross A. Roger, Shen Zengwin and Lavin Gerard J, 64.
26. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 87.
27. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 425.
28. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 425.
29. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 427.
30. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 431.
31. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 433.
32. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 434.
33. Brooks J.D. and Taylor G.H., Carbon, 3 (1965) 185.
34. Brooks J.D. and Taylor G.H., “Chemistry and Physics of Carbon”, Vol. 4, edited by P.L. Walker (Jr.), Marcel Dekkar, Inc., New York, (1968), p. 241.
35. White J.L., "The formation of microstructure in graphitisable carbon", Aerospace Corporation, Air Force Contract No.F0470, 73 C 0074, SAMSO-TR-74-93 , April 15, 1975.
36. Marsh H. and Smith J., “Analytical methods for coal and coal products”, Vol. 2, edited by C. Karr (Jr. Academic Press, New York, 1978), p. 371.
37. Marsh H. and Walker P.L., "Chemistry and Physics of Carbon", Vol. 15, edited by P.A. Thrower (Marcel Dekker, New York, 1979), pp. 229-286.
38. Lewis I.C., Journal de chimie Physique, 81C (1984) 751.
39. Honda H., Carbon, 26 (1988) 139.
40. Donnet J.B. and Voet A., “Carbon Black”, Marcel Decker, New York.

41. PhD. Thesis “ Development of advanced carbon products” by Mishra A.
42. Text book “Introduction to carbon technologies” by Marsh Harry and Heintz A. Edward, 597.
43. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 84.
44. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 85.
45. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 3.
46. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 6.
47. Text book “Polymer Composites” by Gupta M.C. and Gupta A.P, 89.
48 Bhatia G., Aggarwal R. K., Saha M., Sengupta P. R. and Mishra A., Proc. of Nat. Conf. on Carbon, (Indo-Carbon 2001), Vallabh-Vidhyanagar, Gujarat, India, Oct. 19-20, 2001, p. 386.
49. Hoshikawa T. and Nagaoki T., Recent Carbon Technology, English Editor : I.C. Lewis, JEC Press , 1983, p.103.