CHAPTER II

EXPERIMENTAL

AND

CHARACTERIZATION TECHNIQUES
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Introduction

Synthesis of different carbon materials and SiC / Carbon particulate/fiber reinforced composites by different techniques was studied in order to investigate the effect of different ingredients on the microstructure, electrical and mechanical properties. The present work involves:

1. Development of carbon from natural precursors.
2. Microstructures and properties of industrial carbon and graphite.

The processing and characterization of materials and effect on properties were studied using various techniques, and instruments, which are presented in this chapter.

2.1 Raw materials used

Various carbon materials of different composition and types were used as fillers for processing of composites materials. These were derived from (a) natural precursors and (b) processed materials. Synthetic resins/matrix precursor was basically same for all different batches of SiC/Carbon-particulate composites. Carbon from natural precursors and synthetic carbons were first studied for their physical properties before making composites.
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2.2 Carbon material

The present investigations were made on two different types of carbon materials: (1) Carbons from natural precursors and (2) synthetic carbon and composite materials.

2.2.1 Carbon from natural precursors

Carbon as porous materials were made from natural precursors viz., banana fibers, pine wood and coconut fibers through pyrolysis in nitrogen at 1000°C. These carbons were characterized for bulk density, surface area, microstrutural properties, nitrogen adsorption and thermal property. These samples were developed to evaluate the effect on adsorption properties of the samples heat treated at 1000°C. The solid residues obtained were analyzed by classical elemental analysis and were observed by Scanning Electron Microscopy (SEM). There has been a substantive decrease in density and increase in the specific surface area of the treated carbon material because of the effective pore generations.

2.2.2 Synthetic carbon and composite materials

2.2.2.1 Industrial carbon and graphite

Two types of industrial samples were studied namely:

(a) Commercial graphite (b) Manufactured carbons and graphite.

- (a) Commercial graphite: Six samples of commercial graphite were studied and characterized for different properties.

- (b) Manufactured Carbons: Different types of baked carbon, backed carbon & impregnated carbon, graphite carbons with varying types of fillers and heat treated samples provided by Schutz Carbon – Graphite Products, Kalol.
Baked Carbon (BC) is heat treated to a maximum of 1200°C whereas Impregnated and Baked Carbon (PIBC) are impregnated with pitch and are rebaked. Graphite Carbon (GC) is baked to 2500°C - 3000°C.

2.2.2.2 SiC/carbon reinforced particulate composites

(a) Phenolic resin as matrix

The matrix precursor used in this research work was phenolic resin (Novolac type) mixed with 12 % hardener manufactured by Polymers and Polyols Chemicals, Vapi. The novolac phenolic was used as precursor for composite preparation due to its good dimensional stability and high carbon yield. Prime function of phenolic resin was to bind or hold all the ingredients [1]. Phenolic resin is a common binder for resin-based carbon materials. Thermal applications of pure phenolic resins derived carbons are usually limited due to their relatively poor strength. Therefore, it is imperative to incorporate various reinforcing and filling constituents such as reinforcing fibers and fillers into phenolic resin-based composites with the purpose of increasing their strength and stability [2, 3].

Pyrolysis behavior of phenolic resin was studied in N₂ atmosphere at 950°C with heating rate of 20°C/hr as shown in Fig.2.1. During carbonization stage, non-carbon elements in the cured resin come out as volatiles, such as H₂O, CO, CO₂, H₂ and other gases. The reactions were due to the condensation of aromatic ribbon molecules in the cured resin and the volatilization of low molecular weight species. This results in shrinkage and weight loss in the cured resin. The carbon yield of the phenolic resin was found to be (~ 56.74%) which shows it is a good precursor for the carbon-ceramic products.
(b) Silicon carbide powder as filler

SiC was procured from Carbonrundum, Thiruvanathpuram, having purity of 99.9%. The use of SiC material is to enhance the mechanical property of the end product. It has been found that the ceramic particles improve both the room and high temperature strength.

(c) Graphite powder

The natural graphite powder (particle size 1-10 μm) was obtained from M/s Hindustan Electro graphite, Bhopal, India and was used as reinforcing filler.

Natural and synthetic graphite often used to construct the anode of all major battery technologies [3]. The lithium-ion battery utilizes roughly twice more graphite than lithium carbonate [4]. Natural graphite has found uses in zinc-carbon batteries, in electric motor brushes, and various specialized electrical applications. Graphite is also commonly used in the form of powders, and sticks for the purpose of writing or drawing. Graphite of various hardness or softness results in different qualities and properties.
(d) Carbon black as filler

The conductive filler HAF-330 carbon black in the powder form (particle size 2-12 μm) from waste rubber tire was procured from Graphite India Limited, Bangalore and was used for studies in this work. Carbon black particles have the graphite-type crystalline structure, providing excellent electric conductivity [5]. Therefore, carbon black is widely used as conductive filler, being mixed in plastics, elastomer, paints, adhesives, films, and pastes. Carbon black is also used as an excellent antistatic agent [6]. Carbon black also provides stable resistance, and therefore is used as electronic equipment related material in various display components, magnetic recording materials, and OA rolls [7].

(e) Fly ash as filler material

Fly ash was obtained from one of the thermal power station in Gujarat. Fly ash is composed of fine size particles (mean size 10–30 μm) of ceramic. Fly ash particles are typically generated at very high temperatures, i.e. above 1000°C. Hence, these are thermally stable for high-temperature applications and can be used as fillers in carbon particulate composites. Also, majority of fly ash contains substantial amount of silica, alumina, calcium sulfate and unburnt carbon in them, which are already being used in many of the composites fabrication. Fly ash is also readily available at very low cost [8]. Fly ash is a pozzolanic material and has been classified into two classes, Class F and Class C, based on the chemical composition of the fly ash. According to ASTM C 618, the chemical requirements to classify any fly ash are shown in Table 2.1 [9].
Table 2.1: Chemical composition of two different classes of fly ash.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Class F</th>
<th>Class C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO₂) plus aluminum oxide (Al₂O₃) plus iron oxide (Fe₂O₃), min, %</td>
<td>70.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Sulfur trioxide (SO₃), max, %</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Moisture Content, max, %</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Loss on ignition, max, %</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The only difference between class F and class C type is that class F type fly ash contains less than 20 % CaO (calcium oxide), whereas class C contains more than 20% lime. Fig. 2.2 shows typical scanning electron micrograph of fly ash particles. SEM micrograph of fly ash particles shows that most of the particles are spherical in shape. Some of the particles are not spherical. These particles are irregular shaped carbon particles. These are seen in different forms, both anisotropic as well isotropic forms in the fly ash [10].

Fig. 2.2: Scanning electron micrograph of as such fly ash.
(f) Calcined petroleum coke (CPC)

Calcined petroleum coke (CPC) was procured from Schutz Carbon Electrode Private Limited, Kalol, Gujarat. Calcined petroleum coke (CPC), which mainly comprised of graphitic carbons can be used as for carbon composite products for friction applications where low coefficient of friction is required [11]. During carbonization, these also add to the carbon yield. Petroleum coke (often abbreviated Pet coke or pet coke) is a carbonaceous solid derived from oil refinery coker units or other cracking processes. Calcined petroleum coke (CPC) is the product from calcining petroleum coke [12, 13]. The green coke must have sufficiently low metals content in order to be used as anode material.

2.2.3 Carbon fiber reinforced carbon composites

Carbon / carbon composites are a class of materials wherein carbon fibers are reinforced in carbon matrix: (a) Continuous carbon fiber carbon composites and (b) Chopped carbon fiber carbon composites. These composites are high performance composites used in aeromatics as brake pads of aircrafts, in aerospace and other applications requiring use at high temperatures [14].

The macrostructure / microstructure of the carbon matrix and composites play important role in deciding ultimate properties of the composites. Some typical carbon / carbon composites made in the institute as well as obtained from other R&D centers such as advance system laboratory (DRDO) were used to study macro structures / microstructures of the composites.

All the carbon based composites were heat treated to 1000°C also known as carbonization and were characterized for various properties. Carbonization is a thermo-chemical decomposition of organic material at elevated temperatures in the
absence of. It involves simultaneous change of chemical composition and physical phase, and is irreversible [15].

2.3 Processing of various carbon materials

2.3.1 Carbonization of natural precursors

The Carbonization experiments were carried out in a horizontal muffle furnace shown in Fig.2.3 (a). First biomass sample was weighted and placed inside the chamber in heating zone of furnace. Then furnace chamber was made airtight in such a way that air doesn’t get in during carbonization process. For inert atmosphere N₂ gas flow was connected with furnace chamber. The temperature of the furnace was increased as per desired rate using programmable temperature controller. Furnace was heated till chosen carbonization temperature was achieved, and temperature was kept constant for desire time by the temperature controller of furnace. After carbonization and hold time, the furnace was cooled in a programmed way. Lastly, when the temperature of furnace decreased down to room temperature product was taken out, weighed and characterized.

Fig.2.3 (a): Schematic of carbonization set up.
2.3.2 Carbonization of polymer composites to yield carbon matrix composites

Green composites made by hot pressing were carbonized to achieve carbon from phenolic resin. Samples were carbonized in muffle furnace in Nitrogen (N₂) atmosphere at given heating rate. Rate of heating in carbonization depends on raw materials used as carbonaceous source [16]. During carbonization, different volatiles were removed at different temperatures which create pores. Rate of removal of volatiles depend on heating rate of carbonization, so heating rate must be slow to prevent pores formation and chipping of samples [17]. The green composites were then carbonized to 1000°C under inert atmosphere. The arrangement of experimental set up of carbonization process is shown Fig.2.3 (b). The heating rate/cooling rate of SiC/carbon-particulate composites is presented in Fig. 2.4.
Cooling rate during carbonization also plays important role on final properties of sample. If cooling rate is high, it causes bending in samples due to different thermal co-efficient of raw materials used [18].

Logically the simplest way to reduce the manufacturing cost for carbon-carbon composites is to increase the carbonization rate, which is usually very low. However, as in the literature carbonization is primarily a process of pyrolysis of hydrocarbons of a carbon precursor which involves such processes as the cleavage of C–H and C–C bonds, molecular rearrangement, thermal polymerization, aromatic condensation and elimination of side chains (e.g., H₂). To minimize such adverse effects like shrinkage, cracking and thermal stresses that may build up during carbonization, low carbonization/heating rates (typically <10°C/min) are usually required.

Fig. 2.4: Heating rate/cooling rate of SiC/carbon reinforced particulate composites.
2.3.3 General flow chart representing experimental procedure

Fig. 2.5: Carbon particulate composites with variation in filler particles.

2.4 Characterization techniques

Carbon and SiC/carbon particulate / fibrous composites prior to heat treatment and after 1000°C (carbonization) were characterized for physical properties and morphological evaluation. The carbonized samples were characterized for their mechanical, thermal and electrical properties. A major aim of this work was to look at micro structural properties of various samples and relate these to raw materials processing conditions and other related factors.
2.4.1 Physical properties

2.4.1.1 Weight Loss and Volume shrinkage

Heat treatment of various carbon and SiC/carbon-particulate/fibrous composites to 1000°C involves pyrolysis of materials. The process of pyrolysis leads to weight loss and volume shrinkage in the composites. These can be calculated by following equations [19].

\[
\text{Weight loss} = \frac{\text{Initial weight of the sample} - \text{Final weight of the sample}}{\text{Initial weight of the sample}}
\]

\[
\text{Volume shrinkage} = \frac{\text{Initial volume of the sample} - \text{Final volume of the sample}}{\text{Initial volume of the sample}}
\]

Weight measurements and dimensional measurements were performed with precise instruments with micro level sensitivities.

2.4.1.2 Density and porosity

Bulk Density of all composites was calculated according to the ASTM C-838 t-91 which is given by the formula [20]:

\[
\text{Density} (D) = \frac{\text{Weight of composite} [W]}{\text{Volume of composite} [V]} \, \text{gm/cm}^3
\]

Where, \( W \) is the weight of the composite and \( V \) is the volume of the composite. The weighing scale was used to weigh the composites to calculate their apparent density. It is supplied by SHIMADZU and model no. is LIBRORAEG-220 with accuracy of 0.1 mg. bulk density and open porosity (water porosity) of all...
composites were evaluated using Archimedes technique with Metler Toledo AG240 densitometer shown in Fig. 2.6.

Fig. 2.6: Densitometer.

Open porosity and density (kerosene density) were determined by Archimides principle using laboratory set up shown in Fig. 2.7. Both for water porosity and kerosene porosity the samples were dried and evacuated at $10^{-3}$ torr for two hours before putting these for impregnation [21].
2.4.2 Surface morphology

2.4.2.1 Optical microscopy

Optical microscope was used to study the microstructure of reinforcing particles and carbon matrix, fiber/matrix bonding, distribution of reinforcing particles and matrix as well as porosity developed in composites during carbonization. Carbon and carbon composites were embedded in phenolic resin which was then lapped with SiC papers of grades 220, 400, 600, 800, 1000 and 1200. These lapped samples were then polished on Meta serve 2000 polisher using different sized alumina powders of 1 micron, 0.3 micron and 0.05 micron size. After each cycle of polishing, with different grade of powder, the embedded samples were cleaned thoroughly with distilled water in an ultrasonic cleaner (Electronic & Engg. Co., Bombay, Model: Es/250w) till trapped alumina powder is removed. The cleaned samples were dried in the oven at 70°C. These dried samples were then viewed under Leitz Optical Microscope (Fig. 2.8) at different magnification using polarized light.

Fig.2.7: Experimental set up for kerosene porosity measurement.
2.4.2.2 Scanning electron microscopy

The composites were viewed under Scanning Electron Microscope (SEM), Hitachi S-3000N (Fig. 2.9), operated at 30 Kv to ascertain the macrostructures (distribution of fillers, voids, cracks etc.) as well as bonding between carbon matrix and other reinforcements. The carbon-ceramic composites were mounted on graphite adhesive tape, which was then mounted on aluminums stub. This tape acted as both adhesive and conducting material. The samples were then examined at various magnifications to study the reinforcement-matrix bonding, porosity, fillers
distribution, microstructure and surface morphology. Scanning electron microscope was also used to study and analysis of the surfaces of these composite samples.

2.4.3 Nitrogen adsorption studies

The surface characteristics i.e. surface area, pore size, pore size distribution of carbon samples were determined by BET (Brunauer–Emmett–Teller) method using Micromeritics Gemini-2375 surface area analyzer shown in Fig. 2.10. The adsorption of nitrogen gas on to the activated carbon samples was studied at liquid nitrogen temperature (77°K). Prior to adsorption, samples were degassed at temperature up to 250 °C in presence of inert gas argon. The samples were degassed initially at 90°C for one hour and then at 250°C for overnight (14-15 hours). After degassing, the sample was weighed and attached to the surface area analyzer instrument and nitrogen adsorption studies were carried out. The amount of nitrogen gas adsorbed by activated
carbon with respect to relative pressure (P/Po) was obtained in a graphical form called adsorption isotherm. From this adsorption isotherm, the BET surface area, micropore surface area, micropore volume, total pore volume and average pore diameter were obtained [22]. For this, samples were cleaned at 100°C in presence of argon gas for 1 hour and 300 °C for 12 hours.

2.4.4 Thermal characterization

2.4.4.1 Thermal gravimetric analysis

Thermo gravimetric analysis (TGA) is a method of thermal analysis in which changes in weight of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss) [23]. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles. Thermal gravimetric analysis
(TGA) was performed to study pyrolysis behavior of natural precursors, thermosetting resins and polymer matrix composites. Small pieces of samples were loaded in vertical furnace of TGA under the air environment. Heating rate of 20°C/min was maintained during analysis. **Fig. 2.11** shows the photograph of TGA (METTLER TG50 along with Console TC11). TGA was performed to study the pyrolysis behavior of carbonized natural precursors in nitrogen.

![Thermal analysis system](image)

**Fig. 2.11**: Thermal analysis system.

### 2.4.5 Mechanical properties

#### 2.4.5.1 Rockwell (Bulk) hardness measurement

Bulk hardness of carbon materials, composites and SiC / carbon particulate composites were measured using Digital Rockwell Hardness Tester (TRSDM, Balancing Instruments and Equipments, Miraj, India) as shown in **Fig.2.12**, equipped...
with stainless steel ball indenter. Rockwell Hardness values were determined using a hardened steel ball penetrator with a diameter of \( \frac{1}{2}" \) under a major load of 60 Kg/cm\(^2\) (HRR).

Fig. 2.12: Digital Rockwell hardness tester.

Most hardness tests are conducted by penetration techniques and it is finally found that HRR scale is suitable with indenter size of \( \frac{1}{2}" \) ball at load of 60 Kg/cm\(^2\) [24].

The main advantage of digital Rockwell hardness tester is its ability to display digital hardness values directly, thus obviating tedious calculations involved in other
hardness measurement techniques [25]. In order to get a reliable reading, the thickness of the test-piece should be at least 10 times the depth of the indentation. At different five places hardness readings were taken to obtain accurate average readings. Also, readings were taken from a flat perpendicular surface, because convex surfaces give lower readings. [26].

2.4.5.2 Vickers micro hardness analysis (\(H_v\))

The micro hardness of all Sic/carbon particulate composites was measured using Vickers micro-hardness tester by Omni Tech at the room temperature. The Fig.2.13 shows the Vickers microhardness tester.

The Vickers indenter was used with load of 200 gm for 20 s of Dwell time at 100 x magnification. Samples were cut into dimensions of 15X15 mm².

Fig.2.13: Omni Tech Vickers microhardness tester.
Top and bottom surfaces of all SiC/carbon particulate composites were polished by fine sand papers in order to produce a flat surface for the indentation test.

The unit and magnitude of the hardness are defined by Vickers hardness, \( H_v \) and determined by measuring the average diagonal length, \( d \) of the indentation (mm) \[27\], i.e.

\[
H_v = \frac{8F \sin (\phi/2)}{(d_1 + d_2)^2}
\]

Where \( \phi \), \( d_1 \), \( d_2 \) and \( F \) denote the face angle of a pyramidal diamond indenter (136°), two diagonal lengths and test load (N), respectively. The schematic illustration of Vickers hardness testing measurement is shown in Fig.2.14.

\[
d = \frac{(d_1 + d_2)}{2}
\]

Fig.2.14: The schematic illustration of Vickers hardness testing measurement.

2.4.5.3 Compressive measurement

Compressive strength tests were carried out on Instron 5500 machine (Fig. 2.15) having a 150 KN load cell. Crosshead displacement velocities of 0.5 mm/min were maintained for compressive testing. Compressive specimens of 25mm x 15 mm
x 5-6 mm were cut with diamond saw. Crosshead displacement was used to calculate strain in the compression testing [28]. Load and displacement data obtained from Instron Blue hill software was used to calculate stress and strain.

Fig. 2.15: INSTRON Universal Testing Machine.

2.4.6 DC Electrical conductivity of carbon composites (bulk/volume)

Measurements of electrical conductivity/resistivity (volume/bulk) were carried out by Keithley 2400 source meter using four probe techniques to minimize the errors on account of lead wire resistance, contact resistance etc. Customized assembly as per ASTM standard D991 - 89 [29] consists of two current electrodes and two potential electrodes was implemented for measuring DC volume conductivity of samples.
Samples were sandwiched between specific mass (to apply proper pressure) and these electrodes. Required current is applied and voltage drop is measured between potential electrodes. Then resistivity / conductivity was calculated from instrument using data and standard formulas. For proper electrical contact edges of all electrodes applied with silver paint. Typical experimental setup is shown in Fig. 2.16.

**Fig.2.16:** Typical measurement set-up for measurement of electrical conductivity.

The following four probe setup (Fig.2.17) was used for measurement of DC electrical conductivity of long composite samples.
For the electrical conductivity measurements, samples were cut into the size of (130x40x3) mm³ with polished surfaces. Volume or bulk conductivity of all samples was calculated as follows:

\[
\sigma = \frac{1}{\rho}
\]

Where:

\( \sigma \) = volume or bulk conductivity, mho.cm⁻¹,

\( \rho \) = volume or bulk resistivity, Ω.m of the sample which is calculated as:

\[
\rho = \frac{V w d k}{I I}
\]

Where:

\( V \) = potential difference, V, across potential electrodes,
I = current, A, through the current electrodes,

w = width of specimen,

d = thickness of specimen,

l = distance between potential electrodes,

K = factor depending on units in which, w, d, and l are measured; that is, k is 0.001 if w, d, and l are in millimeters.

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