CHAPTER - II

EXPERIMENTAL TECHNIQUES

2.1. INTRODUCTION

The present investigations involved the development of several processing facilities such as resin formation apparatus, compression moulding dies, electrically heated muffle furnaces and testing facilities like electrical resistivity apparatus for glass-like carbons, assembly for the determination of carbon and hydrogen contents etc. The use of some specialised instruments or machines was also made in the present work.

The procedures involved in making these carbons as well as those employed for the determination of their various characteristics, namely, carbonization yield, linear and volume shrinkages, apparent density, water immersion density, kerosene density, open porosity, pore volume and pore size distribution, electrical resistivity, transverse breaking strength, Young's modulus, shore hardness, elemental analysis and scanning electron microscopy have been described in this chapter.

2.2. PREPARATION OF GLASS-LIKE CARBON

The general procedure for the preparation of glass-like carbon is briefly described as follows. Phenol (monohydric or dihydric such as resorcinol and catechol) is reacted with formaldehyde in a particular or range of molar proportions (depending upon the type of phenol used and type of study) at temperatures in the range 50-95°C in the presence or absence
of ammonia catalyst (depending upon the type of phenol used) to get phenol formaldehyde resin which is then densified under partial vacuum in the range 30-40 cm Hg at a temperature of 50-70 °C in the presence or absence of para-toluene sulphonic acid as a hardening catalyst (depending upon the type of phenol used). The resin so obtained is shaped into green artifact by hot pressing and casting techniques and subsequently cured upto 200 °C. The green artifact is then characterized and finally carbonised to 950 °C or higher in the inert atmosphere to get glass-like carbon. The essential steps mentioned above in making glass-like carbon have been summarized in the form of block diagram in Fig.2.1.

2.3. PREPARATION OF RESINS (SIMPLE PHENOL FORMALDEHYDE, CATECHOL FORMALDEHYDE AND RESORCINOL FORMALDEHYDE RESINS)

A requisite quantity of simple phenol (monohydric) is reacted with formaldehyde in different formaldehyde to phenol molar ratios varying between 1.0-3.0 in the presence of ammonia (2-4% by weight of phenol) acting as catalyst under reflux condition till the resin is formed accompanying the separation of an aqueous layer. The glass apparatus used for this purpose is shown diagrammatically in Fig.2.2. The aqueous layer is then removed from the resin. A similar procedure is employed in making catechol formaldehyde resin employing formaldehyde to catechol molar ratio in the range of 1.0-4.0 with the difference that the resin formation temperature is maintained at around 60 °C. In the case of
Fig. 2-1. Block diagram for the preparation of glass-like Carbon.
Fig. 2-2. Resin formation apparatus
resorcinol formaldehyde resin the formaldehyde to resorcinol molar ratio is varied in the range of 1.0-3.0 and the resin is formed at around 50°C in the absence of ammonia catalyst. The resin formation yield is calculated as the percentage weight of the resin formed with respect to the total weight of phenol and formaldehyde taken.

The phenol formaldehyde and catechol formaldehyde resins so obtained are densified at a temperature of 50-70°C under a vacuum of the order of 40 cm Hg in the presence of para-toluene sulphonic acid (normally 2.0% by wt. of the resin) till a honey-like consistency is obtained. The resorcinol formaldehyde resin however does not require the use of above hardening catalyst. During the densification of the resin, water and unreacted volatile matter are removed from the resin. Such a resin is then ready for making green carbon.

2.4. FORMING OF GREEN CARBON

The green carbons are formed from the above prepared resin by two methods, viz, casting method and the hot pressing method.

2.4.1. CASTING METHOD

The hot honey-like clear resin (temperature ~ 70°C) prepared from phenol formaldehyde or catechol formaldehyde or resorcinol formaldehyde is poured into glass tubes (I.D. 3-4 mm, length 150 mm) to prepare rods and steel moulds of different sizes and shapes to prepare cylindrical and conical crucibles of thickness 3 mm and of capacities varying in the range of 10-150 ml. Care is taken to remove bubbles from the moulds by subjecting it to partial vacuum of around 40 cm Hg
at 50-70°C for about 1-2 hrs. Then the resin in these moulds is heated in an oven at about 70°C for 24-72 hrs till it gets completely set. The hardened resin material is taken out of the moulds for further curing. Dental implants and other types of special products are also prepared from their semicured rods by the conventional turning methods on a Lathe machine.

2.4.2. MOULDING METHOD

The phenol formaldehyde resin prepared by the method described above is poured into glass or steel trays which are then semicured in an oven at about 70°C for 48-96 hrs till the resin gets completely set. The hardened resin is then jaw crushed, ground fine in the pulverizer or grinding mill to size finer than 200 B.S. mesh (75.0 μm). The pulverized material is passed through 200 B.S. mesh sieve and the latter is then ready for moulding purposes.

About four grams of the resin powder is then hot pressed into plates of size 60 mm x 20mm x 3 mm using chrome-steel dies kept between heated platens in the conventional compression moulding machine. The experimental set up for moulding green carbon is shown in Fig.2.3. The moulding temperature used ranges from 145-200°C and the pressure applied is 400 kg cm$^{-2}$. Slotted plates of size 60 mm x 20 mm x 3 mm with a slot of size 35 mm x 10 mm x 1.5 mm are also prepared by this method for thin film applications.

2.5. CURING AND CHARACTERIZATION OF GREEN CARBON

Semicured green carbon is finally cured in an oven to a
Fig. 2.3. LABORATORY COMPRESSION MOULDING MACHINE
temperature of 200°C at a rate of 20°C/hr and finally maintained at 200°C for 1 hour. The cured carbons are then cooled to room temperature. After curing, all these plates or rods are characterized with respect to various physical properties like length, volume and apparent green density from the measurement of their dimensions and mass. The density of green carbons in the form of crucibles or other shapes is determined by immersion techniques (using distilled water as the immersion medium).

2.6. CARBONIZATION OF GREEN CARBON

The cured carbon is then packed in a graphite boat using graphite powder as a packing material and is then loaded in a quartz tube having a provision for maintaining an inert atmosphere of UHP nitrogen. The quartz tube containing green carbon is already kept in a muffle tube furnace which can be heated electrically. The green carbon is carbonised to 950°C or higher in nitrogen atmosphere under controlled rate of heating to get defect-free glass-like carbon. The carbonization operation is a very critical operation since the transition from cured resin to glass-like carbon is accompanied by large weight loss (of the order of 30-40%) due to evolution of volatiles and subsequent volume shrinkage (to the extent of 30-45%). The rates of heating chosen in the present studies are 15°C/hr upto 150°C, 6°C/hr from 150°C to 700°C followed by 15°C/hr from 700°C to 950°C or higher temperature as the case may be and final temperature of 950°C or higher is maintained for half an hour and the material is finally cooled to room temperature at the rate of 50°C/hr.
2.7. HEAT TREATMENT UPTO 2600 °C

The glass-like carbons heated at 950 °C or 1100 °C as described above are kept in a graphite boat and then heat treated upto 2600 °C in a graphite tube furnace in an atmosphere of argon gas with a rate of heating of 50 °C/hr. The glass-like carbon material after heat-treatment to 2600 °C or desired temperature is taken out and characterized with respect to several parameters.

2.8. CHARACTERIZATION OF CARBONISED GLASS-LIKE CARBONS

Characterization of glass-like carbons heat treated upto 950 °C or above is done with respect to carbonization yield, linear and volume shrinkages, apparent density, water immersion density, kerosene density, electrical resistivity, transverse breaking strength, Young's modulus, shore hardness, pore volume, pore size distribution and elemental analysis as per the procedures described in the following sub-sections. In general, for the measurements of all the above characteristics ten to fifteen samples are taken.

2.8.1. DETERMINATION OF CARBONIZATION YIELD

The carbonization yield is obtained by the following expression:

\[
\text{Carbonization yield (\%)} = \frac{w}{W} \times 100
\]

where

\[w = \text{weight of heat treated specimen}\]

and

\[W = \text{weight of green carbon specimen}\]
2.8.2. DETERMINATION OF LINEAR SHRINKAGE

The linear shrinkage in the final glass-like carbon product is determined knowing the length of the product in the green and carbonised states. It is given by the expression:

\[
\text{Linear shrinkage (\%)} = \frac{l}{L} \times 100
\]

where

\( l \) = reduction in length of the product after heat-treatment

and

\( L \) = length of green carbon product.

2.8.3. DETERMINATION OF VOLUME SHRINKAGE

The volume shrinkage in a glass-like carbon product after heat-treatment is determined knowing the volume of the carbon product in the green and carbonised states. It is given by the expression:

\[
\text{Volume shrinkage (\%)} = \frac{v}{V} \times 100
\]

where

\( v \) = reduction in volume of the product after heat-treatment

and

\( V \) = volume of the green carbon product.

2.8.4. DETERMINATION OF APPARENT DENSITY

The apparent density of glass-like carbons may be considered as a characteristic of their mechanical structure.
It is determined from the measurements of their mass and dimensions.

2.8.5. DETERMINATION OF WATER IMMERSION DENSITY

Water immersion density is a convenient way of measuring density of glass-like carbons in irregular shapes such as crucibles, tubes, slotted plates etc. The glass-like carbon product is suspended by a thin nylon or synthetic thread on an analytical balance and its weights both in air and in distilled water at a particular temperature are determined. The water immersion density is calculated from the relationship:

\[
\text{Water immersion density} = \left[ \frac{w_1}{w - w_2} \right] \times \rho
\]

where

\[ w_1 \text{ and } w_2 \text{ are the weights of the specimen in air and distilled water respectively.} \]

and

\[ \rho \text{ is the density of distilled water at the temperature of the experiment.} \]

2.8.6. DETERMINATION OF KEROSENE DENSITY

An oven dried sample of given powder material of glass-like carbon is introduced into the weighed specific gravity bottle which is then weighed again. The bottle is then partially filled with kerosene oil such that the sample dips well into the oil. The unstoppered bottle is then placed in a vacuum dessicator and evacuation is started with the help of a vacuum pump. The evacuation is continued until no air bubbles
are observed in the bottle. The remaining space is then filled with kerosene oil up to the full capacity and then weighed. The kerosene density of the material is then calculated by the following expression:

\[
\text{Kerosene density} = \frac{w}{W} \times \rho
\]

where

- \( w \) = weight of the sample
- \( W \) = weight of kerosene oil displaced by the sample
- \( \rho \) = density of kerosene oil.

2.8.7. DETERMINATION OF OPEN POROSITY

Open porosity is obtained by the following expression:

\[
\text{Open porosity (\%)} = (1 - \frac{\text{apparent density}}{\text{kerosene density}}) \times 100
\]

2.8.8. DETERMINATION OF PORE VOLUME AND PORE SIZE DISTRIBUTION

Carlo Erba Strumentazione Mercury Porosimeter Model 200 series was employed to determine pore volume and pore size distribution of glass-like carbon at various stages in the course of its development. A small sample of known mass is inserted in a dilatometer which is then filled with pure mercury using the suction attachment of porosimeter and a double stage rotary pump. Care is taken to see that no air bubbles are entrapped in the dilatometer. The dilatometer assembly is then kept in the autoclave of the porosimeter and
increasing pressure is applied. The diameter \( d \) of the pores into which the mercury penetrates as a result of pressure is given by the following formula:

\[
d(A^o) = 150,000/P
\]  ... (2.1)

where

\[ P = \text{pressure in kg/cm} \]

The mercury porosimeter measures the displacement of the column of the mercury under pressure in the dilatometer by means of contact rod which is then transmitted to the recorder. The displacement along the stem of the dilatometer gives the volume that is filling the pores of the corresponding size at each pressure step. The graph is corrected for the compressibility of mercury by performing a blank test.

The volume \( V \) of pores per gram of the sample at various pressures (corresponding diameters given by equation 2.1) is calculated from the formula:

\[
V = \frac{A \times H}{M}
\]

where

\[ A = \text{dilatometer constant} \]
\[ H = \text{counts transmitted at various pressures} \]
\[ M = \text{mass of the sample} \]

In other words, when the pressure is increased from 1 to 2000 kg/cm the fraction of volume accounted by all pores of sizes between 1,50,000 to 75 A (i.e. pore size
distribution) may be obtained.

2.8.9. **DETERMINATION OF ELECTRICAL RESISTIVITY**

The electrical resistivity is determined by passing a suitable current across the cross-section of the glass-like carbon product placed between two thick copper or brass plates and measuring the potential drop across a known distance along the length of the product with the help of a microvoltmeter using two probes. The apparatus for the determination of electrical resistivity is shown in Fig.2.4.

The electrical resistivity is obtained from the following equation:

\[
\rho = \frac{V}{A} \times \frac{L}{I}
\]

where

- \( \rho \) = resistivity of test specimen
- \( V \) = potential drop across the probe pins
- \( A \) = area of cross-section of specimen
- \( I \) = magnitude of d.c. current
- \( L \) = distance between the probe pins.

2.8.10. **DETERMINATION OF TRANSVERSE BREAKING STRENGTH**

Instron Universal Testing Machine Model 1122 is used to determine the transverse breaking strength of glass-like carbons. The test specimen is kept on two knife edges held at 30 mm (span length) apart. A third movable knife edge available in the testing assembly is brought on to the middle to hold the specimen tight. A slowly increasing load is applied at cross head speed of 5 mm/min on the specimen.
Fig. 2.4. APPARATUS FOR THE DETERMINATION OF ELECTRICAL RESISTIVITY OF GLASS-LIKE CARBONS
through the middle knife edge till the specimen breaks. Stresses so developed in the test are measured with the help of load cell and recorded on a chart. Vertical movement of chart corresponds to the deflection in the carbon. Thus a load versus deflection plot is obtained. Transverse breaking strength is calculated as follows:

\[
\text{Transverse breaking strength} = \left( \frac{3xP \times S}{2xbxt} \right)_{\text{max}} ^ 2
\]

(for plates)

\[
= \left( \frac{8xP \times S}{\pi xd} \right)_{\text{max}} ^ 3
\]

(for rods)

where

\( P_{\text{max}} \) = maximum load arrived by test specimen

\( S \) = span length (30 mm)

\( b \) = width of the specimen

\( t \) = thickness of the specimen

\( d \) = diameter of the specimen.

2.8.11. DETERMINATION OF YOUNG'S MODULUS

Young's modulus is determined from the load versus deflection plot as obtained in the transverse breaking mode of glass-like carbon on the same Instron Universal Testing Machine Model 1122. The Young's modulus is calculated from the formula as given below:

\[
\text{Young's modulus} = \left[ \frac{S^3}{4xbxt} \right] x \frac{p}{d}
\]

where

\( S \) = span length (30 mm)
b = width of the specimen
t = thickness of the specimen
p/d = slope of initial straight line portion of load
deflection curve.

2.8.12. DETERMINATION OF SHORE HARDNESS

The measurement of hardness is of significant importance in several applications of glass-like carbons. In the present investigations, the hardness is measured using a Shore's Scleroscope (made by Coats Machine Tools Co., Ltd., London) which is shown in Fig. 2.5. The method of measurement is based on the dynamic rebound of a diamond tipped hammer falling from a fixed height on the polished surface of the specimen. The rebound height of the hammer gives a measure of the hardness. For the measurement of Shore hardness, the specimen surface may be polished with a medium grit emery paper.

2.8.13. DETERMINATION OF CARBON AND HYDROGEN CONTENT

(PREGL'S METHOD)

The principle of this method is essentially the same as that of the corresponding macro-procedure, i.e., the classical Leibig method in which the sample is heated in a stream of oxygen in presence of an oxidizing catalyst, and the resulting carbon dioxide and water (produced from the carbon and hydrogen, respectively) are absorbed under conditions which enable them to be determined, usually by weighing. Knowing the weights of these products, percentage of carbon and hydrogen can be calculated.
Fig. 2.5. SHORE'S SCLEROSCOPE
(i) EXPERIMENTAL SET-UP

A complete modern Pregl's apparatus set up in the present course of work is shown in Fig. 2.6 and is similar to that recommended in ASTM E-191 specifications.

(ii) PROCEDURE

After assembling the combustion tube and absorption tubes filled with the requisite materials, in the manner described above, the heating of the combustion tube is started in a current of dry oxygen for about half an hour. This drives off any moisture or carbon dioxide from the combustion tube and ensures complete oxidation of the copper oxide. Then water and carbon dioxide absorption tubes are removed and weighed on the microbalance and then again reconnected in the assembly. A platinum boat containing a known weight (about 30 mg) of the moisture-free test substance is then introduced in the combustion tube. Maintaining the copper oxide (wire form) and silver fillings at temperatures of $900 \pm 50 \degree C$ and $550 \pm 50 \degree C$, respectively, the test substance is rapidly heated to a temperature of $500 \pm 25 \degree C$. The heating is continued for about an hour in a slow current of dry oxygen, thereafter the absorption tubes are disconnected from the assembly and quickly weighed again on the microbalance to determine separately the amounts of water and carbon dioxide absorbed. From these observations, the contents of carbon and hydrogen in the test substance are calculated using the following expressions:
FIG. 26 SCHEMATIC REPRESENTATION OF THE APPARATUS FOR THE DETERMINATION OF CARBON AND HYDROGEN CONTENTS
\[
\begin{align*}
\text{Wt. of carbon dioxide} & \quad 12 \\
\text{C (\%)} & = \quad \frac{\text{Wt. of test substance}}{\text{Wt. of test substance}} \times 100 \\
\text{Wt. of water vapours} & \quad 2 \\
\text{H (\%)} & = \quad \frac{\text{Wt. of test substance}}{\text{Wt. of test substance}} \times 100
\end{align*}
\]

2.8.14. SCANNING ELECTRON MICROSCOPY

JEOL Scanning Electron Microscope Model JSM 35 CF is used to observe the surface texture at different stages of heat-treatment. These samples are fixed on the sample holder with the help of silver paste. Silver paste acts as adhesive as well as conducting material. Gold/silver coating is done on the specimen for making it conducting. Specimens are scanned at different angles for various magnifications.