

**SYNTHESIS AND PYROLYSIS OF THERMOSETTING
RESINS**

**A dissertation
submitted in partial fulfillment
of the requirements for the award of degree
of
MASTER OF ENGINEERING
in
Polymer Technology
by
SHEIKH MOHAMMAD MUTIUDDIN
(06/poly/04)**



**DELHI COLLEGE OF ENGINEERING
SHAHBAD-DAULATPUR,
BAWANA ROAD
DELHI-110042**

CERTIFICATE

This is to certify that the project entitled “**Synthesis and Pyrolysis of Thermosetting Resins** ” is being submitted by **Mr. Sheikh Mohammad Mutiuddin**, a student of **Master of Engineering** (Polymer Technology) from Delhi College of Engineering, Delhi was carried out under supervision of Dr. R.C.Sharma, Dr (Mrs.) V.Raman and Dr. G.Bhatia at National Physical Laboratory, New Delhi.

The work embossed in this dissertation is submitted to FOT, UOD for the partial fulfillment of the requirement for the degree of M.E., and has not been submitted to any other university for any degree

The project work was performed during 6th February to 30th June 2006 at NPL, New Delhi.

Dr. V. RAMAN
Scientist ‘F’
Carbon Division,
National Physical Laboratory
New Delhi

Dr. R.C. Sharma
Asst. Professor,
App. Chemistry &
Polymer Technology

Mr. G.BHATIA
Scientist ‘F’
Carbon Division,
National Physical Laboratory
New Delhi

Prof. G.L.Verma
Head
App. Chemistry &
Polymer Technology

ACKNOWLEDGEMENT

I am grateful to many individuals who made their time and knowledge available to help me to work on the “**Synthesis and Pyrolysis of Thermosetting Resins**”.

I sincerely express my deep sense of gratitude to my guide **Dr. R.C.Sharma** Assistant Professor, Delhi College of Engineering, Delhi, for his guidance and supervision, useful discussions and constant encouragement during the course of this project work.

I pay my special gratitude to Dr. (Ms.) V. Raman, “Scientist” ‘F’, of National Physical Laboratory, for providing excellent facilities in their laboratory, continuous encouragement, academic and technical guidance. I am highly thankful to **Dr. G. Bhatia** “Scientist” ‘F’, for her valuable suggestions, kind encouragement, critical interpretations of the results, keen interest in the work and parent like behavior.

I am highly grateful to Dr. Vikram Kumar, Director, NPL, New Delhi, for allowing me to complete my project in this reputed organization.

I am very thankful to Mr. Pinaki Ranjan, Technical Officer “C”, Mr. T. S. Negi, Technical officer “A”, Mr. R.S. Bisht, Technical officer “C” and Mr. Prem Lal, Technical officer “B” for providing me technical help during my project.

In the last, but not the least, I would like to thank my parents for providing their co-operation and encouragement.

(Sheikh Mohammad Mutiuddin)

Content

Page no.

Chapter 1:Introduction

1.1 Thermosets and Thermoplastics	7
1.2 Plastic resins	8
1.2.1 Acetal	8
1.2.2 Acrylics	8
1.2.3 Acrylonitrile-Butadiene-Styrene (ABS)	8
1.2.4 Alkyds	9
1.2.5 Epoxy	9
1.2.6 Fluoropolymer	9
1.2.7 Nylon	10
1.2.8 Phenolic	10
1.2.9 Polyamide-Imide	10
1.2.10 Polyarylates	10
1.2.11 Polycarbonate	11
1.2.12 Polyethylene	11
1.2.13 Polyimides	11
1.2.14 Polyphenylene Oxide, Modified	12
1.2.15 Polyphenylene Sulfide	12
1.2.16 Polypropyl	12
1.2.17 Polystyrene	13
1.2.18 Polyurethane	13
1.2.19 Polyvinyl Acetate (PVAc) & Other Vinyls	13
1.2.20 Polyvinyl Chloride	14
1.2.21 Urea-Formaldehyde	14
1.3 Manufacture of Conventional Carbons	14
1.4 Terminology in Carbon and Graphite Industry	15
1.5 Pyrolysis of thermosetting resin: Preparation of Glassy Carbon	18

Chapter 2: Phenolic Resins

2.1 Introduction	19
2.2 Monomers	20
2.2.1 Phenol	20
2.2.2 Resorcinol	22
2.2.3 Formaldehyde	23
2.3 Polymerization	24
2.3.1 Phenol Formaldehyde	24
2.3.2 Resorcinol Formaldehyde	26

Chapter 3: Glassy Carbon

3.1 Origin of Glass-Like Carbon	28
3.2 Structure of Glass like Carbon	29
3.3 Properties of Glass-Like Carbons	32

Chapter 4: Experimental Techniques for Preparation of Glass-Like Carbon

4.1 Introduction	34
4.2 Preparation of Green Glass-Like Carbon from phenol	
Formaldehyde	34
4.3 Casting Method	36
4.4 Curing and Characterization of Green Carbon	36
4.5 Carbonization of Green Carbon	36
4.6 Preparation of Glass-Like Carbon from Resorcinol	
Formaldehyde	37

4.7 Characterization of Carbonised Glass-Like Carbons	39
4.7.1 Determination of Carbonization Yield	39
4.7.2 Determination of Linear Shrinkage	39
4.7.3 Determination of Volume Shrinkage	40
4.7.4 Determination of Apparent Density	40
4.7.5 Determination of Water Immersion Density	40
4.7.6 Determination of Kerosene Density	41
4.7.7 Determination of Open Porosity	41
4.7.8 Determination of Electrical Resistivity	41
4.7.9 Determination of Transverse Breaking Strength	42
4.7.10 Determination of Young's Modulus	43
4.7.11 Scanning Electron Microscopy (SEM)	44
Chapter 5: Characterization of Glass-Like Carbon	
5.1 Characteristic of Glass-like Carbon from Phenol formaldehyde	46
5.2 Characteristic of Glass-like Carbon from Resorcinol formaldehyde	48
Chapter 6: Experimental Techniques for Manufacture of Bipolar plate	
6.1 Introduction	51
6.2 Techniques to manufacture bipolar plate	53
6.2.1 Coat mix technique	53
6.2.1 Direct mix technique	56
6.3 Molding techniques:	56
6.3.1 Hot molding technique:	56
6.3.2 Cold molding technique	56
Chapter 7: Applications of Glass-Like Carbon	
7.1. Introduction	61
7.2 Glass-Like Carbon Artifacts for Analytical Applications	62
7.2.1. Glass-Like Carbon Crucibles for Silicon Processing	62
7.2.2. Glassy Carbon Resistor Plates and Crucibles for Thin Film Applications	62

7.2.3 Glass-Like Carbon	63
7.2.4 Semi-Conductor Manufacture	66
7.2.5 Acoustic Control	60
7.2.6 Reference Material for Thermal Expansion of Solids	66
Chapter 8: Result and discussion	67
Chapter 9: Conclusion	68
References	69

Chapter 1: Introduction

Polymer may be defined as a large molecule built up by repetition of small, simple chemical units held together by covalent bonds. In some cases, the repetition is linear and chain is built up from its links while others, the chains are branched or interlinked to form three-dimensional network.

The term Plastics has derived from Greek word plastikos that means 'fit for moulding'. Plastics may be defined as a polymer, which are suitable for molding.

1.1 Thermosets and Thermoplastics

The two basic groups of plastic materials are the thermoplastics and the thermosets. Thermoplastic resins consist of long molecules, each of which may have side chains or groups that are not attached to other molecules (i.e., are not crosslinked). Thus, they can be repeatedly melted and solidified by heating and cooling so that any scrap generated in processing can be reused. Usually, thermoplastic polymers are supplied in the form of pellets, which often contain additives to enhance processing or to provide necessary characteristics in the finished product (e.g., color, conductivity, etc.). The temperature service range of thermoplastics is limited by their loss of physical strength and eventual melting at elevated temperatures.

Thermoset plastics, on the other hand, react during processing to form crosslinked structures that cannot be remelted and reprocessed. Thermoset scrap must be either discarded or used as low-cost filler in other products. In some cases, it may be pyrolyzed to recover inorganic fillers such as glass reinforcements, which can be reused. Thermosets may be supplied in liquid form or as a partially polymerized solid molding powder. In their uncured condition, they can be formed to the finished product shape with or without pressure and polymerized by using chemicals or heat.[1]

1.2 Plastic resins

1.2.1 Acetal

Acetal resins are produced by the polymerization of purified formaldehyde [CH₂O] into both homopolymer and copolymer types. Industrial end-users are very familiar with the acetals in the form of gears, bearings, bushings, cams, housings, conveyors and any number of moving parts in appliances, business machines, etc. They also have some special applications such as automotive door handles, seat belt components, plumbing fixtures, shaver cartridges, zippers and gas tank caps. Acetals are extremely rigid without being brittle. They have a high melting point, high strength, good frictional properties and resistance to fatigue. [1]

1.2.2 Acrylics

It is used as lighting diffusers; outdoor signs; automobile tail lights; wash-basins and sinks; safety shields; furniture (e.g., tables); skylights, and large-area enclosures for shopping centers, swimming pools, restaurants, etc., and as room dividers. The outstanding resistance to long-term exposure to sunlight and weathering is one of the more important characteristics of acrylic. [1]

1.2.3 Acrylonitrile-Butadiene-Styrene (ABS)

These families of thermoplastics are called terpolymers, because they are made of three different monomers: Acrylonitrile, Butadiene and Styrene, to create a single material that draws on the best properties of all three. ABS possesses outstanding impact strength and high mechanical strength, which makes it suitable for use in tough consumer and industrial products, including: appliances, automotive parts, pipe, business machines and telephone components. [1]

1.2.4 Alkyds

They are used in liquid form as enamels, paints, lacquers, and similar coatings for automobiles, refrigerators, stoves and similar products--still the largest use for alkyds. Major properties are in the electrical area where alkyd-molding materials offer excellent dielectric strength. Alkyds also have excellent heat resistance and are dimensionally stable under high temperatures. Alkyds are thermosetting unsaturated polyester resins produced by reacting an organic alcohol with an organic acid, dissolved in and reacted with unsaturated monomers such as styrene [$C_6H_5CHCH_2$], or vinyl toluene [$CH_2CHC_6H_4CH_2$]. Typical applications are electrical uses, automotive parts, and as coatings. [1]

1.2.5 Epoxy

They are used for epoxy-glass reinforced plastics are in aircraft components, filament wound rocket motor casings for missiles, pipes, tanks, pressure vessels and tooling jigs and fixtures. Epoxies are also used in the encapsulation or casting of various electrical and electronic components and in the powder coating of metal substrates. Major outlets for epoxies also include adhesives, protective coatings in appliances, industrial equipment, gymnasium floors, etc., and sealants. [1]

1.2.6 Fluoropolymer

Fluoropolymers are known for their inertness to most chemicals, resistance to high temperatures, extremely low coefficients of friction and excellent dielectric properties, which are relatively insensitive to temperature and power frequency. Typical applications for fluoropolymers are electrical/ electronic uses and pipe and chemical processing equipment and non-stick coatings for cookware and other applications. The most common commercial fluoropolymers are: FEP (fluorinated ethylene-propylene), PTFE (polytetrafluoroethylene), PFA (perfluoroalkoxy) and PVF (polyvinyl fluoride). [1]

1.2.7 Nylon

Typical applications for nylons are in automotive parts, electrical/electronic uses, and packaging. Nylon is a generic name for a family of long-chain polyamide engineering thermoplastics which have recurring amide groups [-CO-NH-] as an integral part of the main polymer chain. Nylons are synthesized from intermediates such as dicarboxylic acids, diamines, amino acids and lactams[1]

1.2.8 Phenolic

These thermosetting resins are credited with being the first commercialized wholly synthetic polymer or plastic, and the second major plastic (the first being cellulose nitrate). The basic raw materials are formaldehyde [HCHO] and phenol [C₆H₅OH]. In the uncured and semi-cured condition, phenolic resins are used as adhesives, casting resins, potting compounds, and laminating resins. As molding powders, phenolic resins can be found in electrical uses. They are also used in such applications as: automotive distributor caps, fuse blocks and connectors and appliance handles, knobs and bases. Phenolic is the most popular binder for holding the various plies of wood together in plywood. [1]

1.2.9 Polyamide-Imide

Engineering thermoplastic resins produced by the condensation reaction of trimellitic anhydride [OCC₆H₂C₂O₃] and various aromatic diamines. Typical applications are in the aerospace, automotive and heavy equipment industries. [1]

1.2.10 Polyarylates

They are used for automotive, appliance and electrical applications requiring outstanding heat resistance. They are engineering thermoplastic resins produced by interfacial polymerization of an aqueous solution of the disodium salt of bisphenol A [(CH₃)₂C(C₆H₄OH)₂] with phthalic acid chlorides [C₆H₄(CO)₂Cl₂] in methylene chloride. [1]

1.2.11 Polycarbonate

They are strong, tough and rigid, while having the ductility normally associated with softer, lower-modulus thermoplastics. They also have excellent electrical insulating characteristics, maintained over a wide range of temperatures and loading rates. Polycarbonates are transparent and can be processed in a variety of ways, including injection molding, extrusion, blow molding and rotational molding. Typical applications are glazing, appliances, water bottles and electrical uses. Polycarbonates are engineering thermoplastic resins produced by phosgenation of dihydric phenols, usually bisphenol A $[(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2]$. [1]

1.2.12 Polyethylene

Applications for polyethylenes are packaging films; trash, garment, grocery and shopping bags; molded housewares; toys; containers; pipe; drums; gasoline tanks; coatings and many others. Polyethylenes are thermoplastic resins obtained by polymerizing the ethylene $[\text{C}_2\text{H}_4]$. Low molecular weight polymers of ethylene are fluids used as lubricants; medium weight polymers are waxes miscible with paraffin; and the high molecular weight polymers (i.e., over 6000) are the materials used in the plastics industry. Polymers with densities ranging from about 0.910 to 0.925 are called low density; those of densities from 0.926 to 0.940 are called medium density; and those from 0.941 to 0.965 and over are called high density. The low density types are polymerized at very high pressures and temperatures, and the high density types at relatively low temperatures and pressures. A relatively new type called linear low density polyethylene is manufactured through a variety of processes: gas phase, solution, slurry, or high pressure conversion. [1]

1.2.13 Polyimides

They are used in wire enamels, laminates, adhesives, gears, covers, bushings, piston rings, valve seats, and in solution form as a laminating varnish. Polyimides are characterized by repeating imide linkages: Thermoset polyimides are produced in

condensation polymers that possess reactive terminal groups capable of subsequent cross-linking through an addition reaction. [1]

1.2.14 Polyphenylene Oxide, Modified

Engineering thermoplastic resins produced by the oxidative coupling of 2, 6-dimethylphenol [(CH₃)₂C₆H₃OH] (xylenol), then blended with impact polystyrene. Typical applications are electrical/electronic uses, business machine parts, appliances, and automotive parts. [1]

1.2.15 Polyphenylene Sulfide

Engineering thermoplastic resins produced by the reaction of p-dichlorobenzene [C₆H₄Cl₂] with sodium sulfide [Na₂S]. A thermoplastic, PPS exhibits excellent heat resistance, as well as outstanding chemical resistance, high stiffness and good retention of mechanical properties at elevated temperatures. The major use for polyphenylene sulfide is in electrical/ electronic parts and automotive parts. [1]

1.2.16 Polypropylene

Major applications of commercial PP are packaging, automotive, appliances and carpeting. Polypropylene is made by polymerizing propylene [CH₃CHCH₂] and in the case of copolymers with monomers, with suitable catalysts, generally aluminum alkyl and titanium tetrachloride mixed with solvents. The monomer unit in polypropylene is asymmetric and can assume two regular geometric arrangements: isotactic, with all methyl groups aligned on the same side of the chain, or syndiotactic, with the methyl groups alternating. All other forms, where this positioning is random, are called atactic. Commercial polypropylene contains 90-97% crystalline or isotactic PP with the remainder being atactic. [1]

1.2.17 Polystyrene

Polystyrene is also widely used in other packaging and foodservice products, such as trays, disposable plates, cutlery and tumblers. Other applications include: automotive parts, toys, housewares, appliance parts, wall tiles, radio and TV housings, furniture, floats, luggage and many more. High molecular weight thermoplastic resins produced generally by the free-radical polymerization of styrene monomer $[C_6H_5CHCH_2]$ which can be initiated by heating alone but more effectively by heating in the presence of free-radical initiator (such as benzoyl peroxide $[(C_6H_5CO)_2O_2]$). [1]

1.2.18 Polyurethane

They are extremely versatile plastics in terms of the forms in which they are available: flexible or rigid foams, solid elastomers (or rubbers), coatings, adhesives and sealants. Their versatility also extends to chemical structure in that, although the urethanes are generally considered to be thermosets, there are grades of urethane elastomers that are thermoplastic in nature and are supplied in pellet form for molding, calendaring and extrusion. In the presence of a blowing agent, this reaction will produce a foamed material having excellent thermal insulating properties and is widely used in building insulation. The foams can either be soft and flexible or tough, and rigid, with all the possible variations in-between. They are used in furniture, cushioning, carpet underlay, bedding, packaging, textiles and automotive seating and safety padding. Rigid foams offer outstanding insulating values, excellent compressive strength, good dimensional stability and buoyancy. In the form of elastomers, polyurethanes offer superior abrasion resistance and toughness, and are used in applications in which good performance and long service life are important: printing rolls, gaskets and seals, cable insulation, drive and conveyor belts, solid tires and automotive applications. [1]

1.2.19 Polyvinyl Acetate (PVAc) & Other Vinyls

Polyvinyl acetate is a thermoplastic resin produced by the polymerization of vinyl acetate monomer $[CH_3COOCHCH_2]$ in water producing an emulsion with a solids

content of 50-55%. Typical applications for the above resins are adhesives, paints, coatings and finishes, and packaging. [1]

1.2.20 Polyvinyl Chloride

Vinyls are used mainly for their chemical and weathering resistance, high dielectric properties, or abrasion resistance. Vinyl is also dip molded into gloves, slush molded into boots and foamed to make calendered flooring, leather-like upholstery, shoe fabrics and carpet backing. Vinyls are thermoplastic resins produced by the polymerization of the gas vinyl chloride [CH_2CHCl]. Under pressure, vinyl chloride becomes liquid and can be polymerized by suspension, emulsion, bulk, or solution polymerization. The pure polymer is hard, brittle and difficult to process, but it becomes flexible when plasticizers are added. A special class of PVC resin of fine particle size, often called dispersion grade resin, can be dispersed in liquid plasticizers to form plastisols. The addition of a volatile diluent or a solvent to the plastisol produces an organosol. [1]

1.2.21 Urea-Formaldehyde

Urea-Formaldehyde is a very hard, scratch-resistant material with good chemical resistance, good electrical qualities and heat resistance up to 170 degrees F. Urea-Formaldehyde resins are formed by the condensation reaction of formaldehyde [HCHO] and urea [$\text{CO}(\text{NH}_2)_2$]. These thermoset resins are clear water-white syrups or white powdered materials which can be dispersed in water to form colorless syrups. They are used as laminates and chemically resistant coatings. [1]

1.3 Manufacture of Conventional Carbons

As the graphite-liquid-gas triple point of the element carbon is close to 4020 K at a pressure of 125 atmospheres, the process of melting and casting normally used in metals is inapplicable to carbon. Consequently, the bulk of carbon and graphite is manufactured by a process analogous to the powder metallurgy. It will, however, be useful at this stage to introduce briefly the important steps involved in the manufacture of carbon and graphite products.

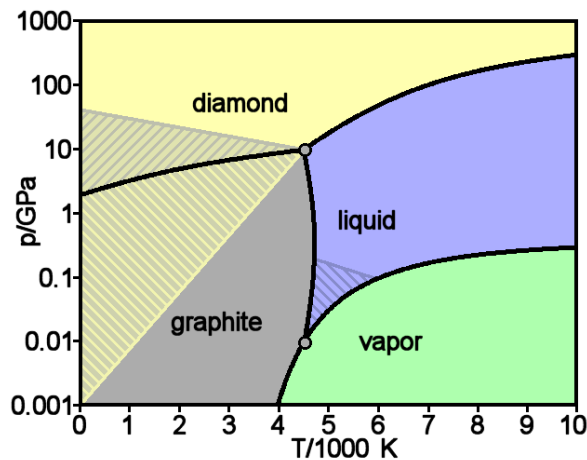


Fig 1: Basic phase diagram of carbon, which shows the state of matter for varying temperatures and pressures. The hatched regions indicate conditions under which one phase is metastable, so that two phases can coexist

The conventional carbon products are manufactured mainly from a mixture of carbonaceous solid material such as petroleum coke, pitch coke, metallurgical coke, anthracite coal, carbon black, natural graphite etc. and a carbonaceous binder material, for example, coal tar pitch. The mixture after being pressed into a product of desired shape and size is fired in a non-oxidizing atmosphere to a temperature of 900 to 1800°C. Products in this form are widely used. However, for many applications, such a carbon product is further heat treated to a temperature of 2600°C.

1.4 Terminology in Carbon and Graphite Industry

As is the case in many industries, the carbon and graphite industry has a language of its own. The terms ‘carbon’, amorphous carbon, baked carbon, industrial carbon, or manufactured carbon are used by the industry to mean products, made from the mixture of suitable carbonaceous filler and binder materials, which have been baked to a temperature of 900-1800°C. The term green carbon refers to the formed carbonaceous product which has not been baked. The term graphite, electrographite, synthetic graphite, or industrial graphite refers to a product obtained from the heat-treatment of the baked soft carbon at a temperature of 2400°C or higher.

However, recently the scope of the terms Carbon and graphite has been reviewed by IUPAC International Committee on Characterization and Nomenclature

of Carbon and Graphite. According to this committee, the term carbon refers to those materials possessing an atomic C/H ratio of at least 10 and the term graphite refers to such carbons which have acquired the near-ideal structure of graphite. The term carbon thus comprises all types of cokes and (Acheson) electrographite, all types of polycrystalline carbons and graphites, all types of active carbons, all types of carbon blacks and all natural graphites etc. among the common varieties. Special varieties of carbon have increased in number in recent years and include pyrolytic carbon and pyrolytic graphite, graphite foils and felts, all types of carbon fibres as well as glass-like carbon.

Table 1: Physical Properties of Conventional Carbon and Graphite Products

Characteristics	Conventional Baked Carbon	Carbon Products Graphitized Carbon
Density (g cm ⁻³)	1.5-1.7	1.55-1.75
Permeability (cm ² /sec)	10-100	1-10
Porosity (%)	12-35	12-40
Thermal conductivity (cal/cm/sec/°C)	0.01-0.02	0.25-0.5
Coefficient of linear thermal expansion (x 10 ⁻⁶ /°C)	1-5	0.4-4.5
Specific heat (Cal/g/°C)	0.20	0.17
Compressive strength (MPa)	43-62	12-59
Transverse breaking strength (MPa)	14-42	14-28
Tensile strength (MPa)	6-8	3-14
Young's modulus (GPa)	11-16	3-12
Electrical resistivity (m ohm cm)	3.5-5.0	0.7-1.3
Crystal structure	Two dimensional Turbostratic structure	Three dimensional Graphite structure
Max. use temperature (°C)	Air 350	Inert 2500 Air 425

1.5 Pyrolysis of thermosetting resin: Preparation of Glassy Carbon

The pyrolysis of thermosetting resins in an inert atmosphere at high temperature (1000-1400°C) results Glass-like carbon is a new carbon material, which combines some of the properties of glass, namely, lusture, imperviousness and mode of fracture, with the other physical and chemical properties of carbon. It is being produced in various shapes and sizes from a variety of thermosetting resins under different trade names by various manufacturers. Glassy Carbon is a non-porous, non-reactive form of carbon which also posses some properties of glass. Cellulose, phenol formaldehyde, polyfurfuryl alcohol, acetone furfural, aromatic resins such as naphthalenediol and other polymer resins have been cited as precursory materials for this carbon.

Its chief characteristics such as high strength and hardness, high resistance to corrosion and erosion, low porosity and permeability make glass-like carbon a versatile material in a wide range of analytical, metallurgical, mechanical, electrical, electronics and biomedical applications.

Glassy carbon artifacts find numerous applications in form of crucibles, beakers and other vessels, components of ovens etc., suitable for high temperature application in inert atmosphere and harsh environments (zone melting, monocrystals preparation, decomposition by acids etc.). Important utilization is in analytical electrochemistry. Glass-like carbons can be developed by the controlled carbonization of one of a variety of polymeric materials.

Chapter 2: Phenolic Resins

2.1 Introduction

Phenolic resins are a large family of polymers and oligomers, composed of a wide variety of structures based on the reaction products of phenols with formaldehyde. Phenolic resins are employed in a wide range of applications, from commodity construction materials to high technology applications in electronics and aerospace industries. Generally, but not exclusively, thermosetting in nature, phenolic resins provide numerous challenges in the areas of synthesis, characterization, production, product development, and quality control.

As a family of resins originally developed in the early twentieth century, the nature and potential of phenolic resins have been explored thoroughly. Phenolic resins are prepared by the reaction of phenol or substituted phenol with an aldehyde, especially formaldehyde, in the presence of an acidic or basic catalyst. Their thermosetting character and the exotherm associated with the reaction presented technical barriers to commercialization. In 1900, the first U.S. patent was granted for a phenolic resin, using the resin in cast form as a substitute for hard rubber [3].

Early phenolic resins consisted of self-curing, resole-type products made with excess formaldehyde, and novolaks, which are thermoplastic in nature and require a hardener. The early products produced by General Bakelite were used in molded parts, insulating varnishes, laminated sheets, and industrial coatings. These areas still remain important applications, but have been joined by numerous others such as wood bonding, fiber bonding, and plywood adhesives.

2.1 Monomers

2.1.1 Phenol

Phenol, also known under an older name of carbolic acid, is a colorless crystalline solid with a typical sweet tarry odor. Its chemical formula is C_6H_5OH and its structure is that of a hydroxyl group (-OH) bonded to a phenyl ring; it is thus an aromatic compound.

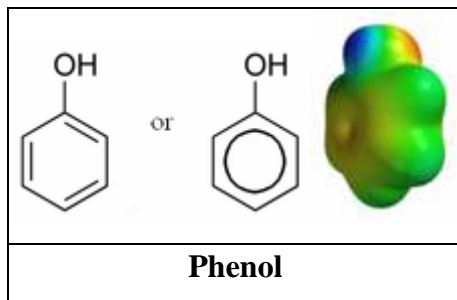


Fig 2: Structure of phenol

The word phenol is also used to refer to any compound which contains a six-membered aromatic ring, bonded directly to a hydroxyl group (-OH). In effect, phenols are a class of organic compounds of which the phenol discussed in this article is the simplest member.[2]

Properties

Phenol has a limited solubility in water (8.3 g/100 ml). It is slightly acidic: the phenol molecule has weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$. Compared to aliphatic alcohols, phenol shows much higher acidity. This is due to the mesomeric effect.[2]

Uses

- The primary use of phenol is in the production of phenolic resins, which are used in the plywood, construction, automotive, and appliance industries.

- Phenol is also used in the production of caprolactam and bisphenol A, which are intermediates in the manufacture of nylon and epoxy resins, respectively. [2]

Table 2: Properties of Phenol

Properties	
Density	1.07 g/cm ³
Solubility in water	8.3 g/100 ml (20 °C)
Melting point	40.5 °C
Boiling point	181.7 °C
Acidity (pK _a)	9.95
Chemical formula	C ₆ H ₅ OH
Molar mass	94.11 g/mol
Appearance	White Crystalline Solid
Flash point	79 °C
Autoignition temperature	715 °C

Other uses of phenol include as a disinfectant, and in medicinal products such as ear and nose drops, throat lozenges, and mouthwashes.

2.1.1.3 Health Hazard Information

Phenol and the substituted phenols are hazardous in nature and should be handled with utmost care. [2]

2.1.1.4 Substituted Phenols

Phenol itself is used in the largest-volume, but substituted phenols are used for specialty resins (Table-3). Substituted phenols are typically alkylated phenols made from phenol and a corresponding α -olefin with acid catalysts[3]. Acidic catalysis is frequently in the form of an ion-exchange resin (IER) and the reaction proceeds preferentially in the para position. For example, in the production of t-butylphenol using isobutylene, the product is >95% para-substituted. The incorporation of alkyl phenols into the resin reduces reactivity, hardness, cross-link density, and color formation, but increases solubility in non-polar solvents, flexibility, and compatibility with natural oils.

Table 3: Substituted Phenols used for Phenolic resins

Substituted phenol	Resin application
Cresol {o-, m-, p-}	coatings, epoxy hardeners
p-t-butylphenol	coatings, adhesives
p-octylphenol	carbonless paper, coatings
p-nonylphenol	carbonless paper, coatings
p-phenylphenol	carbonless paper
bisphenol A	low color molding compounds, coatings
resorcinol	adhesives
cashew nutshell liquid	friction particles

2.1.2 Resorcinol

The meta (1,3) isomer of dihydroxybenzene is resorcinol (also known as resorcin), which forms clear needle crystals used in the production of diazo dyes and plasticizers. It is produced by sulfonating benzene with fuming sulfuric acid and fusing the resulting benzene disulfonic acid with caustic soda. Resorcinol is used in resins as an UV absorber. It is used in manufacturing fluorescent and leather dyes and adhesives. Reaction with formaldehyde produces resins (resorcinol formaldehyde resins) used to make rayon and nylon. It is used as a pharmaceutical to treat acne and other greasy skin conditions in combination with other acne treatments such as sulfur. It is used as an anti-dandruff agent

in shampoo and sunscreen cosmetics. It is also used as a chemical intermediate to synthesis pharmaceuticals and other organic compounds. The para (1,4) isomer is hydroquinone (also known as quinol), which forms clear prisms used as a photographic reducer and developer (except in color film). It is formed in large quantities by chemical reduction of benzoquinone. [4]

Table 4: Properties of Resorcinol

Properties	
Physical state	White to off-white needle crystals
Melting point	110 - 113 c
Boiling point	280 c
Specific gravity	1.272
Solubility in water	Completely soluble
Vapor density	3.8
Autoignition	608 c
Flash point	127 c
Stability	Stable under ordinary conditions
pH	5.2

2.1.3 Formaldehyde

In one form or another, formaldehyde is used almost exclusively in the production of phenolic resins, regardless of the type of phenol. Although formaldehyde is a gas at room temperature, it is readily soluble in water, and it is most commonly sold as a 37% solution in water called by trade names such as formalin or formol.[5].

2.2 Polymerization

2.2.1 Phenol Formaldehyde

Phenol is reacted with Formaldehyde (taken in ratio of 1:1.3) in the presence of Ammonia (2% by weight of phenol) as a catalyst. The mixture is then boiled at a temperature of 70°C along with N₂ stirring. The mixture is heated till a resinous mass (Novolac) is obtained. Phenolic novolaks are thermoset resins having a molecular weight of 500-5000 and a glass-transition temperature, T_g, of 45-70°C.

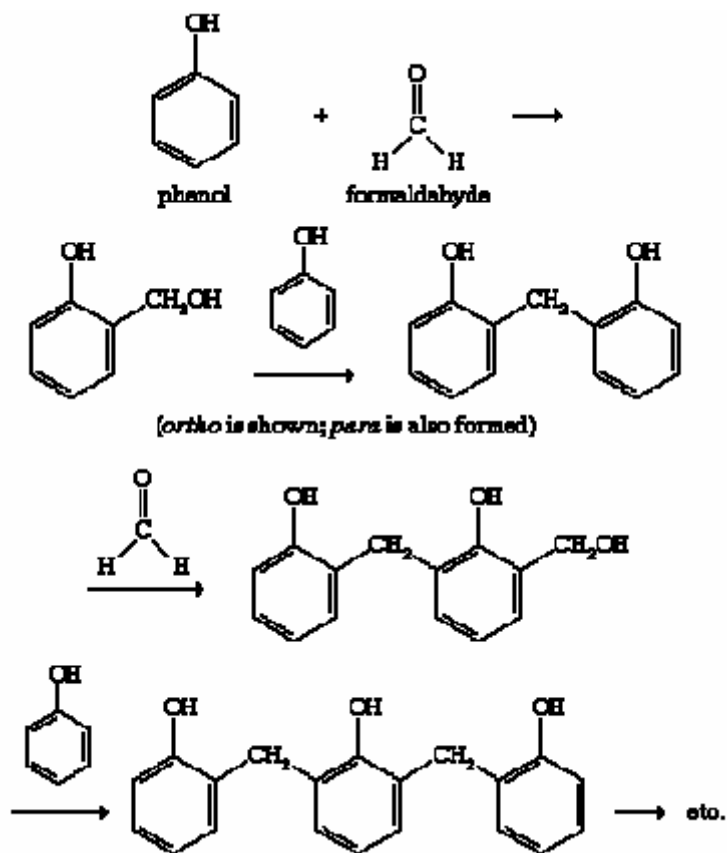


Fig 3: Molecular representation of polymerization of resorcinol with formaldehyde

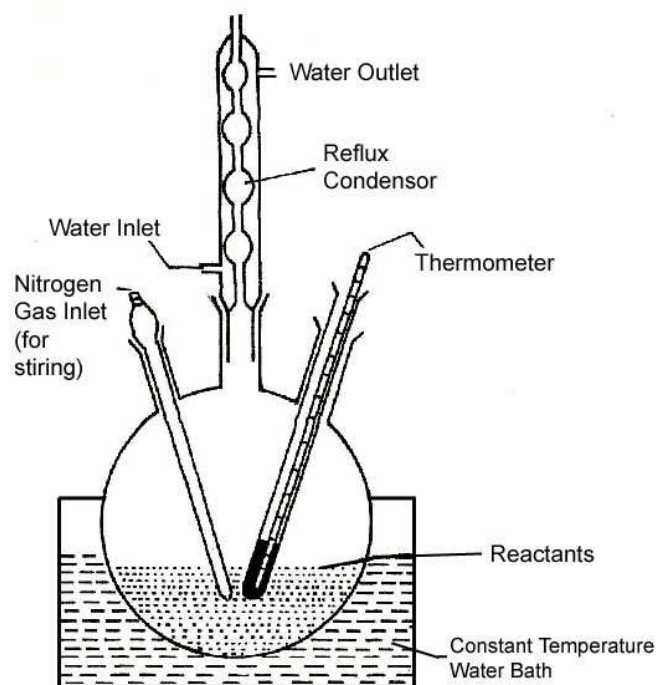


Fig 4: Apparatus used for PF synthesis

Densification of phenol formaldehyde resin

The phenol formaldehyde resin obtained can be densified under partial vacuum at a temperature of 60°C in the presence of p-toluene sulphonic acid (2% by weight of the resin). The instance at which the resin becomes jelly-like can be used for moulding and casting purposes.

Applications

- ❖ Coatings
- ❖ Dispersions
- ❖ Adhesives
- ❖ Carbonless copy paper
- ❖ Molding compounds
- ❖ Abrasives
- ❖ Friction materials

- ❖ Foundry resins
- ❖ Laminates
- ❖ Air and Oil filters
- ❖ Wood bonding
- ❖ Fiber bonding
- ❖ Composites
- ❖ LIM
- ❖ Fibers

2.2.3 Resorcinol Formaldehyde

Resorcinol is reacted with formaldehyde (taken in the ratio of 1:1.5). The reaction takes place at 60°C alongwith constant stirring and didn't require any catalyst. The reaction time is around 2-3 hours. The resorcinol-formaldehyde resin has very short uncured life and cured suddenly as soon as the polymerization is complete and hence, it cannot be stored. For moulding purposes, the reaction mixture should be directly poured into the moulds when it becomes resinuous.

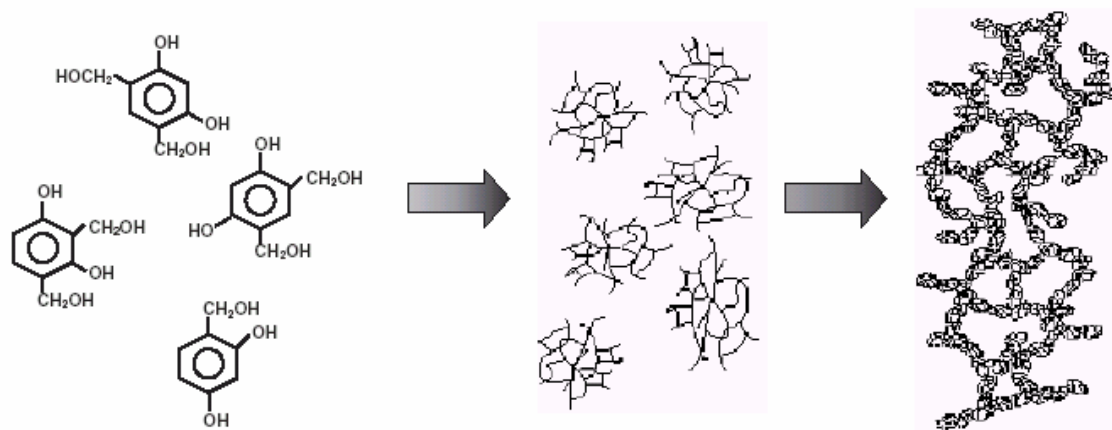
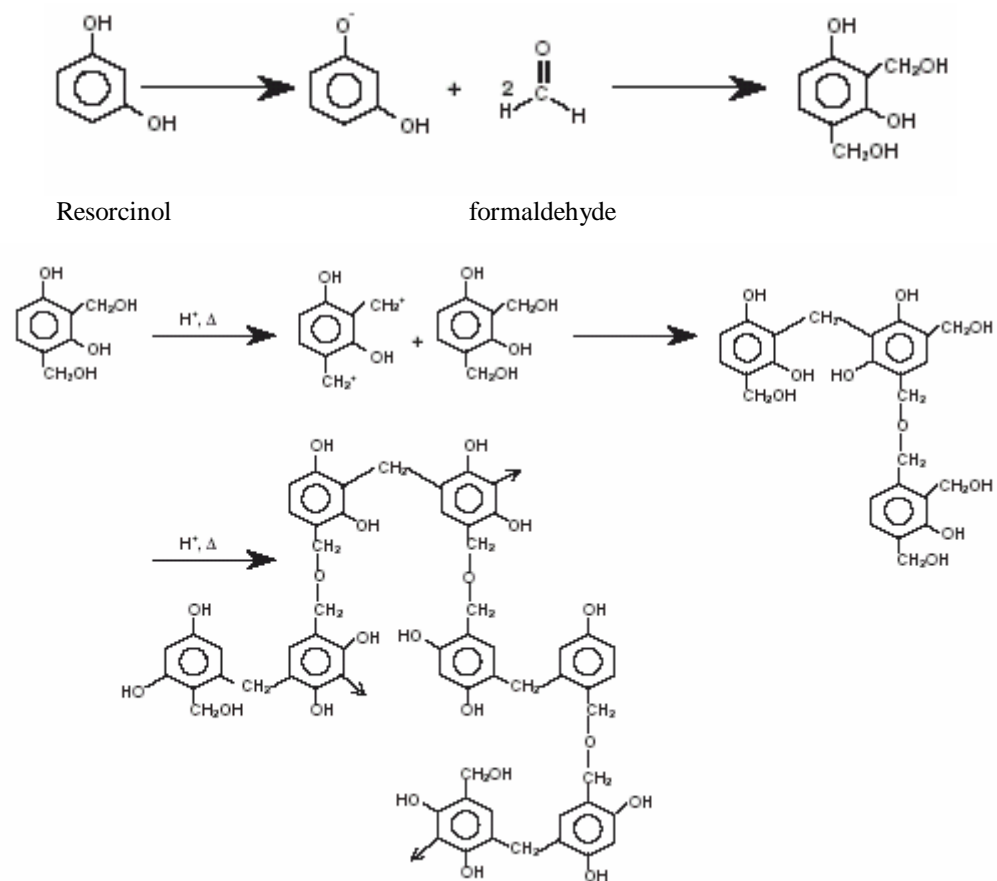


Fig 5: Molecular representation of polymerization of resorcinol with formaldehyde

Chapter 3: Glassy Carbon

3.1 Introduction

The widespread use of graphitic carbons in electrochemical systems is due to their high electrical conductivity, good corrosion resistance, and reasonable mechanical and dimensional stability. Specific applications of graphitic carbons include electrodes, electro-catalyst supports, and bipolar electrode separators. Because of the high ash content of natural graphites, most graphitic carbons used in electrochemical applications are synthesized from hydrocarbons. A unique feature of synthetic graphites is the wide variety of microstructures accessible, depending upon the source of the carbon precursors and the method of preparation.

Of these various forms of carbon, glassy carbon (GC) has been widely used as an electrode. Glassy carbon derives its name from exhibiting fracture behavior similar to glass, from having a disordered structure over large dimensions (although it contains a graphitic microcrystalline structure), and because it is a hard shiny material capable of high polish.

In the early sixties, there was a great need of impermeable carbon, thermally stable from 1000-2000°C for use as a sheath material for fuel elements in the development of high temperature gas-cooled reactors. Industrial development of impregnation as a means to obtain impermeable carbon seems to have lagged, perhaps due to the difficulty in obtaining homogeneous impermeability. As a consequence of it, two methods for the preparation of impermeable carbon were proposed and developed nearly at the same time, one by Yamada and Sato [6] and the other by Davidson[7] and both carbons had interesting impermeable properties. Although these carbons were found to have adequate impermeability, their behavior under irradiation was however observed to be unsatisfactory for the purpose. Since then, efforts have been continuing to explore other applications of this carbon. As a result, glass-like carbons in various shapes and sizes have been developed. Numerous publications have also appeared in the literature concerning this carbon.

Yamada et al[8] and Lewis and coworkers[9, 10] have described the properties and applications of this form of carbon without regard to its method of production. Cellulose[7, 11], phenol formaldehyde[12-16], polyfurfuryl alcohol[17], acetone furfural[18], aromatic resins such as naphthalenediol[19] and other polymer resins have been cited as precursory materials for this carbon. Fitzer and coworkers have presented an exhaustive account of the chemistry of formation and the properties of glass-like carbon made from polyfurfuryl alcohol and phenol formaldehyde resins and the mixtures thereof, and have noticed that all of these lead to glass-like carbons with essentially the same physical properties. Good reviews on this form of carbons have been published by Yamada[20], McKee[21] and recently by Jenkins and coworkers[22, 23]. However, it has been noticed that these reviews also do not provide much information on the manufacturing aspect of this form of carbon. The glass-like carbon artifacts are being manufactured by only few firms in the world and their processes are still a closely guarded secret.

The current approach to the conventional preparation of glassy carbon solids involves the careful pyrolysis of one of a variety of polymeric materials, including polyvinyl chloride, poly(vinylidene chloride), cellulose, phenolic resin poly(furfuryl alcohol), and polyacrylonitrile.

3.2 Structure of Glass like Carbon

The formations of impermeable glass-like carbon by thermal decomposition of cross-linked polyfurfuryl alcohol, phenolic resins and mixtures thereof, have been studied in detail by Fitzer et al. It was found by them that the characteristics of the final glass-like carbons were independent of chemical structure of these resins. In all cases, a bulk density of 1.5 g/cm^3 was obtained which in comparison to bulk density of graphite appeared to give 30% of porosity. The electron micrographs of ruptured surfaces of glass-like carbon however showed no pores whereas the carbonization of industrial raw material (resin unknown) to produce glass-like carbon showed pores with diameter from 2-20 micrometer with maximum pore formation at 800°C .

Micropore volume of the various resin syst Ray small angle scattering carried out on samples heat-treated to 1200°C revealed a uniform porosity of 25Å and of 35Å after heat-treatment to 3000°C.

The first ever model for the structure of glass-like carbon was proposed by Noda and Inagaki. They studied radial distribution of X-ray diffraction and suggested it to be comprising of small graphite like turbostratic crystallites joined together in a random manner by extensive tetrahedral C-C bonds of diamond type. Takahashi and Westrum on the other hand suggested that glass-like carbon had a two-dimensional layer structure from the measurements of specific heat of this carbon at low temperatures wherein they found that the specific heat was proportional to the square of the ambient absolute temperature.

Jenkins et al have also described the structure of glass-like carbon by direct pyrolysis of phenolic resins (phenol hexamine mixtures). It was observed that most important chemical changes during pyrolysis were the formation of intermolecular cross-links at 350°C due to modification of methylene bridges. This was in agreement with the results of Ouchi and Fitzer and Schaefer. This process resulted in the formation of aromatic ribbon molecules. The development of parallel extensive sheets of graphite is prevented in the system because continuity is preserved along the length of each ribbon by strong carbon-carbon bonds, which are to be broken to produce extensive areas of graphite sheets. The three-dimensional structure model as proposed by them for isotropic glass-like carbon is illustrated in Fig.3.1 which consists of twisted bent and intertwined microfibrils comprising stacks of narrow graphite ribbons. The fibrils are held together with covalent interfibril links of strength lower than that in the ribbon themselves. No amount of heating below 3000°C will transform the polymeric carbon into a graphitic carbon because of the enormous activation energies required to produce free carbon atoms, once locked in a polyaromatic complex. It is probable that closed micropores are present in such a structure which account for the low observed density of this carbon. Cowlard and Lewis[21] have reported the apparent size-of crystallites as 75Å (La) x 28Å (Lc) with ems reached a maximum at 700°C. The X- Ray small angle scattering carried out on

samples heat-treated to 1200°C revealed a uniform porosity of 25Å and of 35Å after heat-treatment to 3000°C.

The first ever model for the structure of glass-like carbon was proposed by Noda and Inagaki. They studied radial distribution of X-ray diffraction and suggested it to be comprising of small graphite like turbostratic crystallites joined together in a random manner by extensive tetrahedral C-C bonds of diamond type. Takahashi and Westrum on the other hand suggested that glass-like carbon had a two-dimensional layer structure from the measurements of specific heat of this carbon at low temperatures wherein they found that the specific heat was proportional to the square of the ambient absolute temperature.

Jenkins et al have also described the structure of glass-like carbon by direct pyrolysis of phenolic resins (phenol hexamine mixtures). It was observed that most important chemical changes during pyrolysis were the formation of intermolecular cross-links at 350°C due to modification of methylene bridges. This was in agreement with the results of Ouchi and Fitzer and Schaefer. This process resulted in the formation of aromatic ribbon molecules. The development of parallel extensive sheets of graphite is prevented in the system because continuity is preserved along the length of each ribbon by strong carbon-carbon bonds which are to be broken to produce extensive areas of graphite sheets. The three dimensional structure model as proposed by them for isotropic glass-like carbon is illustrated in Fig-6 which consists of twisted bent and intertwined microfibrils comprising stacks of narrow graphite ribbons. The fibrils are held together with covalent interfibril links of strength lower than that in the ribbon themselves. No amount of heating below 3000°C will transform the polymeric carbon into a graphitic carbon because of the enormous activation energies required to produce free carbon atoms, once locked in a polyaromatic complex. It is probable that closed micropores are present in such a structure which account for the low observed density of this carbon. Cowland and Lewis have reported the apparent size-of crystallites as 75Å (La) x 28Å (Lc) with an interlayer spacing of 3.44 Å compared with many hundreds of Å for a typical electrode graphite.

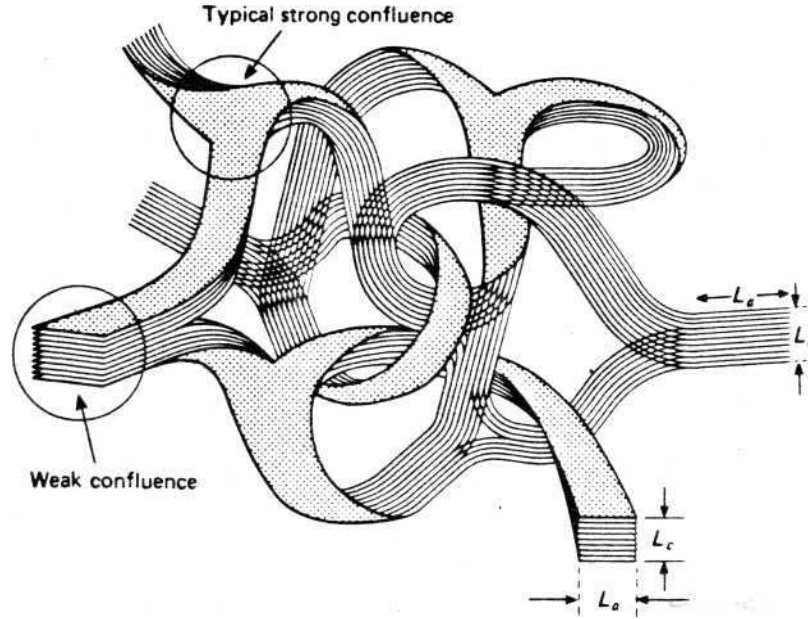


Fig 6: Three Dimensional Structural Model for Glass-Like Carbon

3.3 Properties of Glass-Like Carbons

It has been stated that the glass-like carbon is obtained by the carbonization of certain cross-linked polymers such as cellulose, phenol formaldehyde and polyfurfuryl alcohol under carefully controlled conditions and that the characteristics of glass-like carbons so obtained are essentially independent of the nature of the starting materials. The physical characteristics of glass-like carbon in comparison to those of conventional carbons have been summarized in table-5. The most striking differences between glass-like carbons and the conventional graphites are their extremely low permeability to gasses and the closed micro porosity. The very low open micro porosity of glass-like carbon in spite of low values of density compared to graphites indicates that the pores in glass-like carbon are either extremely small or completely closed for all practical purposes. As a result, a glass-like carbon tends to be more chemically inert than the conventional form of carbons. Besides this, the glass-like carbon possesses much higher strength and hardness than the conventional carbons. It has electrical resistivity 3 to 8 times that of graphite electrode, and as a result the glass-like carbon can also be considered as a conductive ceramic. Glass-like carbon is resistant to chemical attack by a variety of corrosive materials as it does not

react with nitric, sulphuric, hydrofluoric or chromic acids at temperatures sufficient to cause rapid attack on graphites.

Table 5: A Comparison of the Typical Characteristics of Glass like Carbon with Conventional Graphite

Characteristic	Glass-Like Carbon	Conventional Graphite
Apparent density (g cm ⁻³)	1.45-1.55	1.55-1.75
Open porosity (%)	<0.05	12-40
Gas permeability (cm ² /sec)	2.5x10 ⁻¹¹ (He)	1-10
transverse breaking strength (MPa)	100-140	14-28
Young's modulus (GPa)	25-30	3-12
Electrical resistivity (m ohm cm)	5-10	0.7-1.3
Thermal conductivity (Cal/cm sec °C)	0.01-0.02	0.25-0.50
Coefficient of thermal expansion (x10 ⁻⁶ /°C)	2-3.5	2-4
Crystallite size (HTT = 2750°C)	La = 75 A ⁰ Lc = 28 A ⁰ d = 3.44 A ⁰	La = 1000 A ⁰ Lc = 600 A ⁰ d = 3.36 A ⁰
Max. Use temp. (°C)	Inert 2500 Air 550	Inert 2500 Air 425

Chapter 4: Experimental Techniques for Preparation of Glass-Like Carbon

4.1 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 etc.

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 and electrical resistivity, transverse breaking strength, Young's modulus, and scanning electron microscopy have been described in this chapter.

4.2 Preparation of Green Glassy Carbon from phenol formaldehyde

The general procedure for the preparation of glass-like carbon from phenol formaldehyde resin is briefly described below. Phenol is reacted with formaldehyde in a particular or range of molar proportions (depending upon the type of phenol used) at temperatures in the range 50-95°C in the presence 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 (moulding) and casting techniques and subsequently cured up to 180°C. The green artifact is then characterized and finally carbonized 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-7.

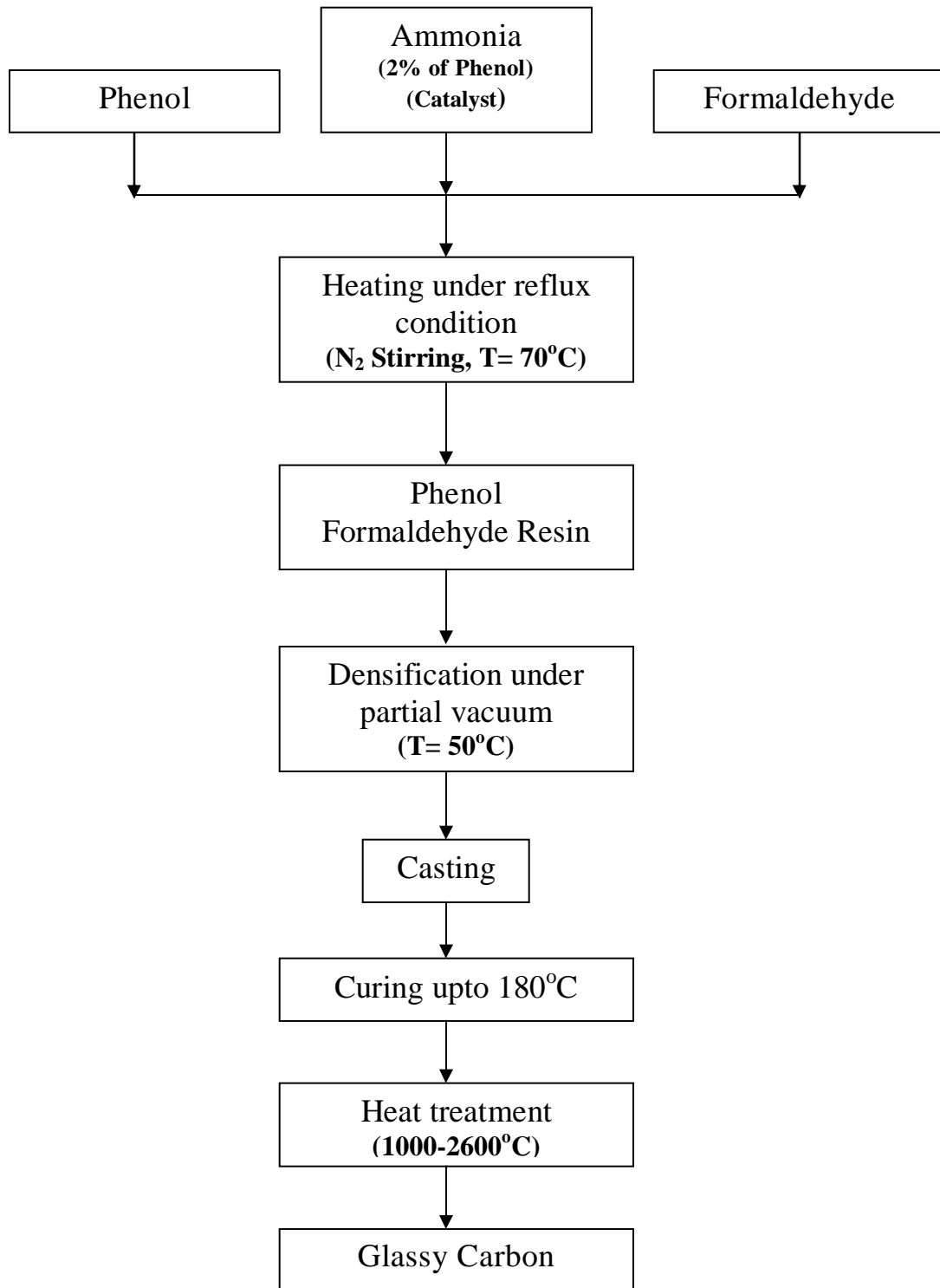


Fig 7: Block Diagram of the manufacture of Glassy Carbon from Phenol Formaldehyde resin

4.3 Casting Method

The hot honey-like clear resin (temperature~70°C) prepared from phenol 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.

4.4 Curing and Characterization of Green Carbon

Semi cured green carbon is finally cured in an oven to a temperature of 180°C at a rate of 10°C/hr and finally Maintained at 180°C for 1hour. 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).

4.5 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 carbonized to 1000°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 is 10°C/hr upto 1000°C and final temperature of

1000°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.

4.6 Preparation of Glass-Like Carbon from Resorcinol Formaldehyde

Resorcinol and Formaldehyde are reacted at a temperature of around 55-60°C in a optimum ratio of 1:1.5 along with constant stirring for about 2-3 hours. As soon as, the reaction mixture becomes viscous, it is directly moulded or casted. Care should be taken to avoid bubbles in the moulds and in case of bubbles are found in the moulds, they are subjected to partial vacuum of around 40 cm Hg at 50-70°C for about 1-2 hrs to remove the bubbles. 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 at 1000°C by the same procedure as used for Phenol Formaldehyde.

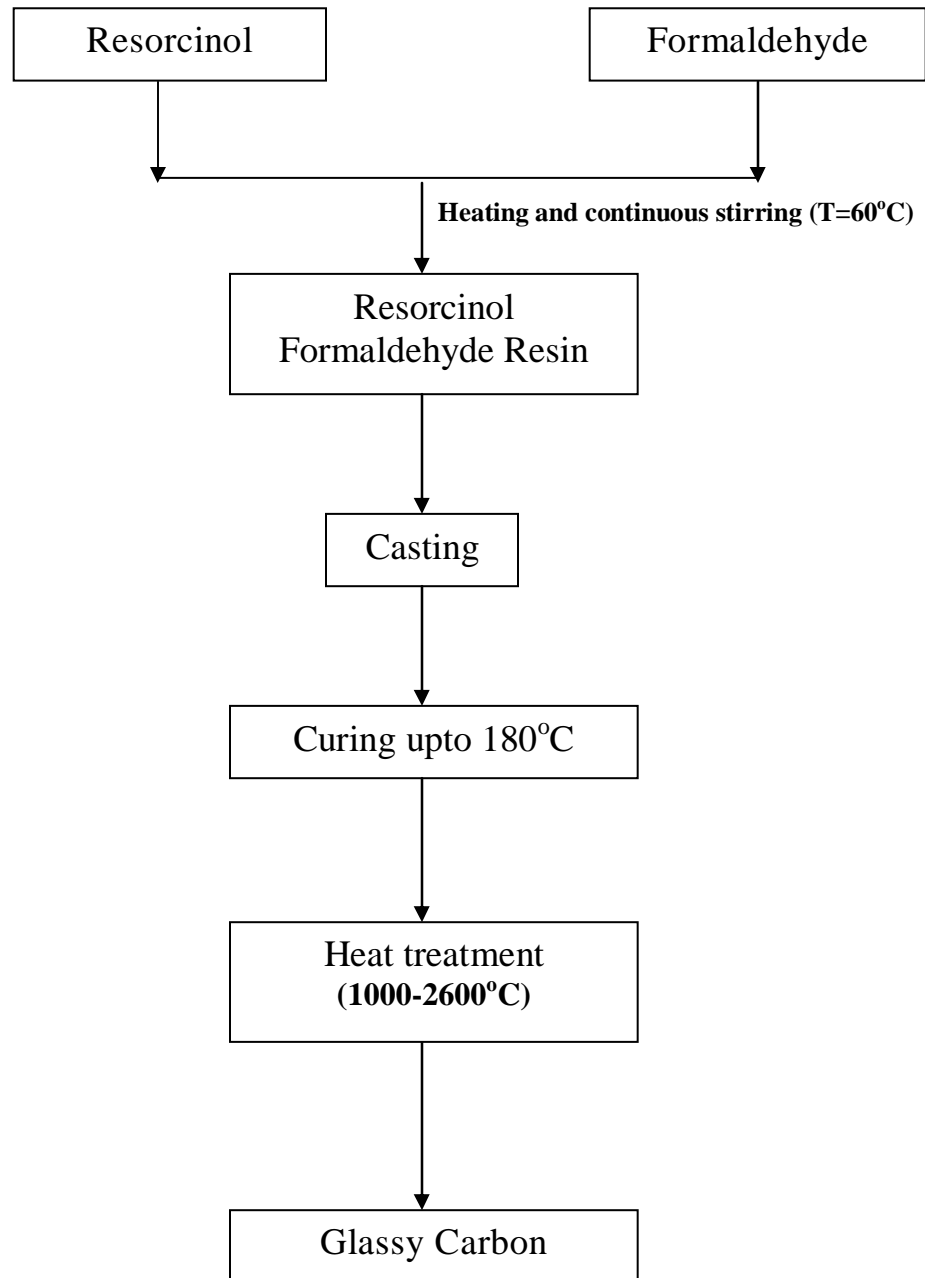


Fig 8: Block Diagram of the manufacture of Glassy Carbon from resorcinol Formaldehyde resin

4.7 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 as per the procedures described in the following sub-sections:

4.7.1 Determination of Carbonization Yield

The carbonization yield is obtained by the following expression:

where

w = weight of heat treated specimen and

W = weight of green carbon specimen.

$$\text{Carbonization yield (\%)} = w/W \times 100$$

4.7.2 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 carbonized states. It is given by the expression:

$$\text{Shrinkage (\%)} = l/L \times 100$$

where

l = reduction in length of the product after heat-treatment and

L = length of green carbon product.

4.9.3 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 carbonized states. It is given by the expression:

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

Where

v = reduction in volume of the product after heat-treatment and

V = volume of the green carbon product.

4.9.4 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.

4.9.5 Determination of Water Immersion Density

(Archimedes Principle)

Water immersion density is 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:

$$\text{Water immersion density} = [w_1 / (w_1 - w_2)] \times \rho$$

Where,

w₁ and w₂ are the weights of the specimen in air and distilled water respectively.

And ρ is the density of distilled water at the temperature of the experiment.

4.9.6 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 upto the full capacity and then weighed. The kerosene density of the material is then calculated by the following expression:

$$\text{Kerosene density} = w/W \times \rho$$

Where

w = weight of the sample

W = weight of kerosene oil displaced by the sample and

ρ = density of kerosene oil.

4.9.7 Determination of Open Porosity

Open porosity is obtained by the following expression:

$$\text{Open porosity (\%)} = (1 - \text{apparent density} / \text{kerosene density}) \times 100$$

4.9.8 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.4.4. The electrical resistivity is obtained from the following equation:

$$P = (V/I \times A/L)$$

Where

P = 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.

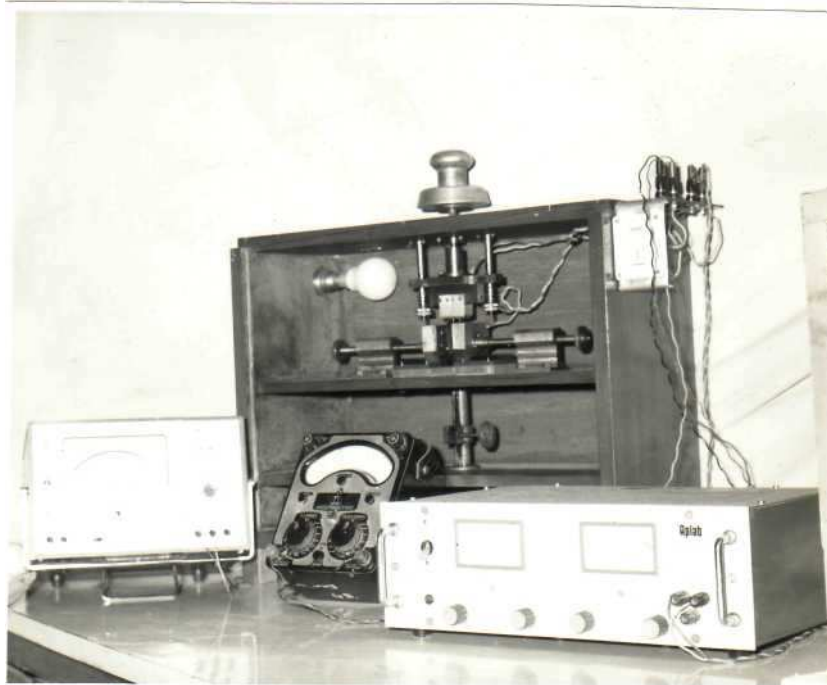


Fig 9: Apparatus for the Determination of Electrical Resistivity

4.9.9 Determination of Transverse Breaking Strength

Instron Universal Testing Machine Model 4411 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 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:

For Plates

$$\text{Transverse breaking strength} = (3P_{\max} \times S) / (2 \times b \times t^2)$$

For Rods

$$\text{Transverse breaking strength} = (8P_{\max} \times S) / (\pi d^3)$$

where

P_{\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.

4.9.10 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 4411. The Young's modulus is calculated from the formula as given below:

$$\text{Young's Modulus} = [S^3/4bt^3] \times p/d$$

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.

4.10 Scanning Electron Microscopy (SEM)

The SEM image is formed by scanning a finely focused electron beam across the sample surface. The electron beam and specimen interaction produce secondary electron emission and electron-induced x-ray fluorescence. The instrument is highly sensitive to surface morphology because low-energy electrons escape only from the upper atomic layers. These escaping electrons are detected and used in the image-forming process. Because of the high surface sensitivity of the electrons, the spatial resolution is excellent. The average SEMs routinely attain a lateral spatial resolution of less than 100 Å. Recent instrument advances have improved the resolution capability of the instrument.

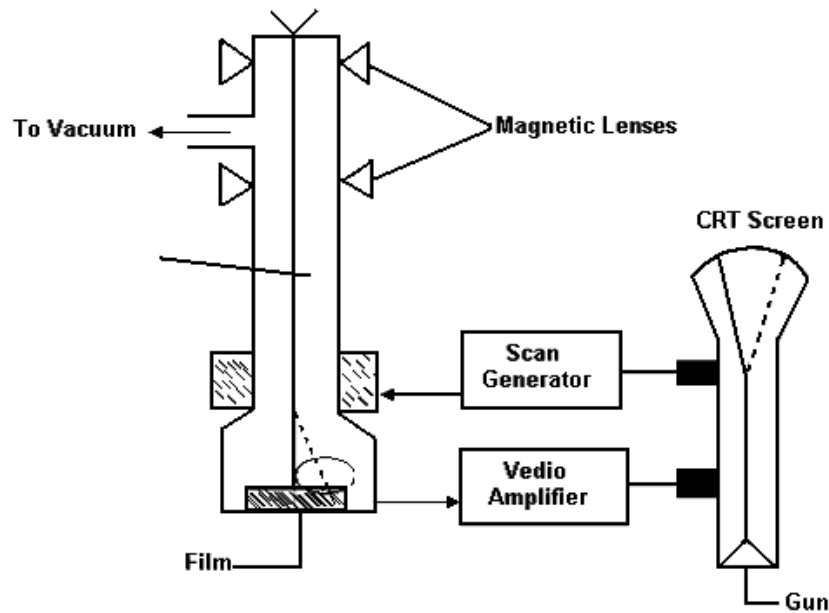


Fig 10: Schematic diagram of Scanning Electron Microscopy (SEM)



Fig 11: A Photograph of the SEM Apparatus

Chapter 5: Characterization of Glass-Like Carbon

5.1 Characteristics of Glass-like Carbon from Phenol formaldehyde

Phenol formaldehyde resin synthesized glass like Carbon showed average green density of 1.25g/cm^3 whereas average bulk density came out to be 1.49g/cm^3 . The carbonization yield was calculated to be 62% which attributes the cross linking of resin molecules due to methylene bridges. Volume shrinkage of 48% and linear shrinkage 19% owe to the evolution of volatiles during pyrolysis. The simultaneous changes in carbonization yield, volume shrinkage and green density are consequences of increase in bulk density and decrease in total porosity. The transverse breaking strength and modulus of the prepared phenol formaldehyde resin based glassy-carbon are found to be 288 Mpa and 22.8 GPa respectively. The open porosity of the glassy carbon is found to be very low (2%) along with average kerosene density of 1.51g/cm^3 .

The characteristics of green and carbonized samples of phenol formaldehyde resin are shown in table 6,7 & 8:

Table 6: Characteristics of Green Glassy Carbon Rods Synthesized from Phenol-Formaldehyde

Sample No.	Radius	Length	Volume	Mass	Green Density
1	0.1450	5.089	0.336	0.422	1.256
2	0.1523	5.453	0.397	0.488	1.229
3	0.1524	2.837	0.207	0.257	1.240
4	0.1427	3.901	0.243	0.313	1.256
5	0.1515	6.091	0.439	0.545	1.241
6	0.1493	6.294	0.441	0.552	1.252
7	0.1518	3.784	0.274	0.340	1.243

Table 7: Characteristics of Baked Glassy Carbon Rods Synthesized from Phenol-Formaldehyde

Sample No.	Radius	Length	Volume	Mass	Baked Density
1	0.1154	4.110	0.172	0.256	1.491
2	0.1203	4.382	0.199	0.298	1.498
3	0.1209	2.294	0.105	0.155	1.471
4	0.1150	3.154	0.131	0.193	1.472
5	0.1215	4.953	0.230	0.344	1.499
6	0.1210	5.110	0.235	0.348	1.485
7	0.1220	3.079	0.144	0.215	1.500

Table 8: Weight loss, Radial& Linear Shrinkage, Volume Shrinkage and Carbonization Yield of Phenol Formaldehyde heat treated to 1000°C

Sample No.	Weight Loss	Radial Shrinkage	Linear Shrinkage	Volume Shrinkage	Carbonization Yield
1	39.33	20.41	19.23	48.80	60.66
2	38.93	21.01	19.64	49.87	61.07
3	39.69	20.67	19.14	49.27	60.31
4	38.34	19.41	19.14	46.09	61.66
5	36.88	19.80	18.68	47.60	63.11
6	36.96	18.30	18.81	46.71	63.04
7	36.75	19.6	18.63	47.44	63.23

The surface morphology of the glass like carbon synthesized from Phenol Formaldehyde system was determined by SEM (Leo 440) and the micrographs is given in fig-12. It is seen from the micrographs that there is no cracks and voids present at the surface and this explains the impermeability, good mechanical and electrical properties obtained with the phenol-formaldehyde resin based glass like carbon.

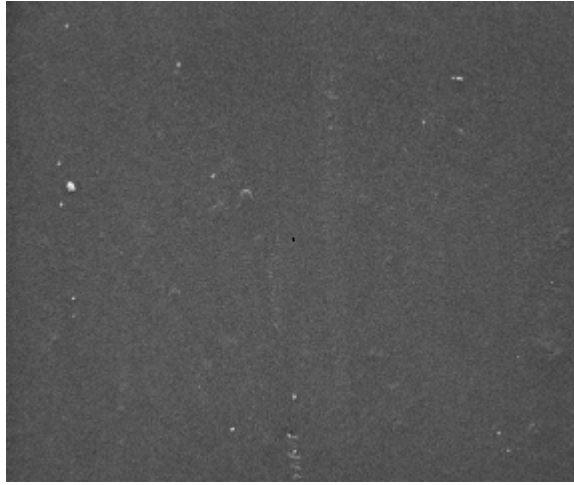


Fig 12: Scanning Electron Microgram (SEM) of glassy carbon made from Phenol Formaldehyde resin

5.2 Characteristics of Glass-like Carbon from Resorcinol Formaldehyde

Resorcinol formaldehyde resin synthesized glass like Carbon showed average green density of 1.20g/cm^3 whereas average bulk density came out to be 1.45g/cm^3 . The carbonization yield was calculated to be 59.6% which attributes the cross linking of resin molecules due to methylene bridges. Volume shrinkage of 50% and linear shrinkage 20.5% owe to the evolution of pyrolysis products. The simultaneous changes in carbonization yield, volume shrinkage and green density are consequences of increase in bulk density and decrease in total porosity. The transverse breaking strength and modulus of the prepared phenol formaldehyde resin based glassy-carbon are found to be 233 Mpa and 23.7 GPa respectively. The open porosity of the glassy carbon is found to be lower than glassy carbon obtained from phenol formaldehyde (1.5%) along with kerosene density of about 1.455 g/cm^3 .

The characteristics of green and carbonized samples of phenol formaldehyde resin are shown in table 9, 10 & 11:

Table 9: Characteristics of Green Glassy Carbon Rods Synthesized from Resorcinol-Formaldehyde

Sample No.	Radius	Length	Volume	Mass	Green Density
1	0.1503	7.179	0.509	0.604	1.187
2	0.1524	7.338	0.535	0.631	1.179
3	0.1517	5.631	0.407	0.488	1.199
4	0.1265	6.989	0.351	0.420	1.194
5	0.1506	5.970	0.425	0.503	1.183
6	0.1533	8.216	0.606	0.723	1.193
7	0.1310	7.324	0.395	0.496	1.256
8	0.1565	8.479	0.652	0.809	1.241
9	0.1575	8.533	0.665	0.833	1.252
10	0.1546	8.680	0.654	0.823	1.259
11	0.1550	7.064	0.533	0.670	1.257
12	0.1550	8.625	0.651	0.818	1.256
13	0.1562	7.227	0.554	0.715	1.291

Table 10: Characteristics of Baked Glassy Carbon Rods Synthesized from Resorcinol-Formaldehyde

Sample No.	Radius	Length	Volume	Mass	Green Density
1	0.1184	5.689	0.250	0.361	1.443
2	0.1189	5.809	0.258	0.378	1.460
3	0.1200	4.467	0.202	0.291	1.439
4	0.0982	5.534	0.168	0.250	1.494
5	0.1184	4.719	0.208	0.300	1.446
6	0.1211	6.508	0.300	0.431	1.435
7	0.1036	5.888	0.198	0.293	1.488
8	0.1256	6.806	0.337	0.487	1.445
9	0.1257	6.840	0.339	0.497	1.464
10	0.1243	6.891	0.339	0.492	1.453
11	0.1226	5.674	0.268	0.400	1.496
12	0.1226	6.927	0.333	0.488	1.466
13	0.1256	5.797	0.287	0.424	1.479

Table 11: Comparative Properties of Baked Glassy Carbon Vs Green Glassy Carbon Produced from Resorcinol-Formaldehyde

Sample No.	Weight Loss	Radial Shrinkage	Linear Shrinkage	Volume Shrinkage	Carbonization Yield
1	40.23	21.22	20.76	50.88	59.77
2	40.1	21.98	20.84	51.77	59.91
3	40.37	20.90	20.67	50.36	59.63
4	40.48	22.37	20.82	52.14	59.52
5	40.36	21.38	20.95	51.06	59.64
6	40.39	21.00	20.79	50.50	59.61
7	40.92	20.92	19.61	49.88	59.07
8	39.80	24.43	19.73	48.31	60.20
9	40.34	20.19	19.85	49.02	59.67
10	40.22	19.60	20.61	48.17	59.78
11	40.30	20.90	18.40	49.72	59.70
12	40.34	20.90	19.69	49.85	59.66
13	40.70	19.59	19.79	48.20	59.30

The surface morphology of the glassy carbon synthesized from Resorcinol Formaldehyde system was determined by SEM (Leo 440) and the micrographs is given in fig-14. It is seen from the micrographs that there is no cracks and voids present at the surface and this explains the impermeability, good mechanical and electrical properties obtained with the resorcinol-formaldehyde resin based glass like carbon.

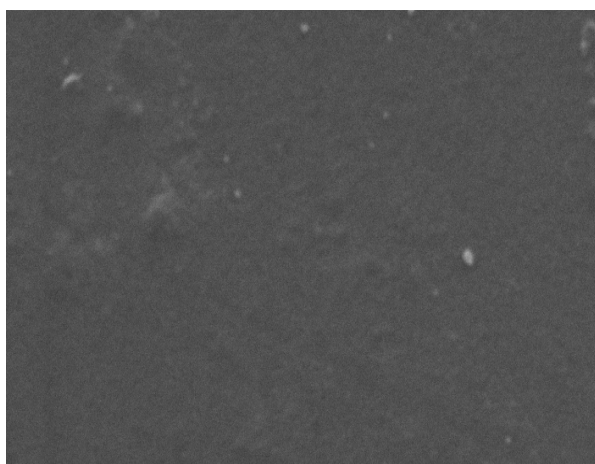


Fig 14: Scanning Electron Microgram (SEM) of glassy carbon made from Resorcinol Formaldehyde resin

Chapter 6: Experimental Techniques for Manufacture of Bipolar plate

6.1 Introduction

The phenolic resin employs in the fabrication of the bipolar plates in the fuel cell because of their better binding and carbonization properties. The fuel cell is an electrochemical device that enables the direct and efficient conversion of chemical energy stored in the fuel along with an oxidant into electrical energy. Although discovered more than 160 years ago, fuel cells have recently attracted the attention of energy consuming devices manufacturers. This is due to the advantages that fuel cells offer over other energy consuming devices. However, the widespread commercialization of the technology has not been made possible due to the high cost of the fuel cell system. The advantages that accrue with the use of fuel cells outweigh their commercialization issues. Consequently, a lot of R&D efforts are going on within virtually every major automobile and power industry and in different universities around the world. The biggest challenge to the development of polymer electrolyte membrane (PEM) fuel cell type for automotive applications is the reduction in cost of the fuel cell stack components (bipolar/end plate, catalyst and electrolyte membrane). The final component on the outside of the fuel cell is the end (collector) plate, which contains a gas flow-field on one side and is flat on the other side. The fuel cell current is drawn from the flat side of the plate. The bipolar (separator) plate provides a separation between the individual fuel cells whose function is to provide a series of electrical connections across different cells in the fuel cell stack and to direct fuel and oxidant gas streams to individual cells. The overall efficiency of the fuel cell depends on the performance of the bipolar/end plates in the fuel cell stack. Conventionally, these plates are made out of graphite with machined gas flow-field channels. Graphite plates are good performers; however, the machining process required to make flow-field channels in these plates is quite expensive, and consequently, alternative materials and concepts are required to fabricate these plates.

Bipolar/end plate is one of the most important and costliest components of the fuel cell stack and accounts to more than 80% of the total weight of the stack. Bipolar plates have to accomplish many functions in the fuel cell stack.[24]

Main functions are:

1. Distribution of fuel gas and air uniformly over the active areas.
2. Heat removal from the active area.
3. Conduction of current from cell to cell.
4. Preventing leakage of gasses and coolant.

For uniform gas distribution, tight tolerances on channel dimensions have to be met. Small deviations lead to reduced efficiency, reduced power output and poor gas utilization and should therefore be avoided. Heat removal requires preferably integrated cooling channels. To minimize ohms losses the material needs to have low bulk resistance, and low contact resistance. The material may not contain components that can poison the membrane and catalysts.

The main materials are:

1. electro graphite.
2. carbon–carbon composite.
3. sheet metal.
4. flexible graphite foil.
5. graphite polymer composite.

High purity electro graphite is an excellent material for machining prototype plates, but material costs and process costs are generally considered to high for mass production.

Carbon–carbon composite is not expected to achieve ambitious cost price targets, and needs expensive post processing (CVI). Sheet metal, graphite foil and graphite polymer composites are potentially low cost materials, and in principle suitable for mass production. In this chapter, the development of graphite composite is explained. **.[25]**

6.2 Techniques to manufacture bipolar plate

6.2.1 Coat mix technique

The initial experiments examined the concept of coating filler grains by the droplets of a binder emulsion. Such an emulsion is formed if a dissolved binder is injected into a second liquid, the so-called precipitation liquid. In forming the emulsion and coating of filler grains, the following criteria had to be taken into consideration:

(i) The filler has to be insoluble in the solvent of the binder and the precipitation liquid.

In the case of carbon filler materials these conditions are normally fulfilled.

(ii) The binder has to be soluble in the solvent, which is consolute with the precipitation liquid.

(iii) The binder has to be insoluble or nearly insoluble in the precipitation liquid.

Coating

Initially, different kinds of binder and feasible systems of solvents and precipitation liquids were investigated. Of course, economic reasons and the fact that the reproducibility of phenol formaldehyde (PF) resins is much better than that of pitches led to the decision to make all further investigations with PF resins. Two different procedures were developed: the “solvent process” and the “base-acid process”.

The first process uses a solution of binder in a solvent, e.g. alcohol, and water as the precipitation liquid. The second process is based on a solution of PF resin in an aqueous alkali, e.g. soda liquor, and acidified water as the precipitation liquid.

Fortunately, conditions were found under which filler grains were coated with binder and nearly no free binder could be detected in the slurry. This fulfilled an important aim of the mixing process of filler grains with binder, namely the homogeneous distribution of filler and binder in the mixture.

Solvent process.

After dissolving the binder in an alcohol, which is miscible with water, the filler powder is added and, by stirring, a suspension is formed. The real mixing follows as the suspension is poured under stirring into the precipitation liquid, during which time the binder precipitates and coats the filler particles, and the alcohol consolute scale. A

disadvantage of the process may be the with the water (Fig. 15). salinity of the waste water.

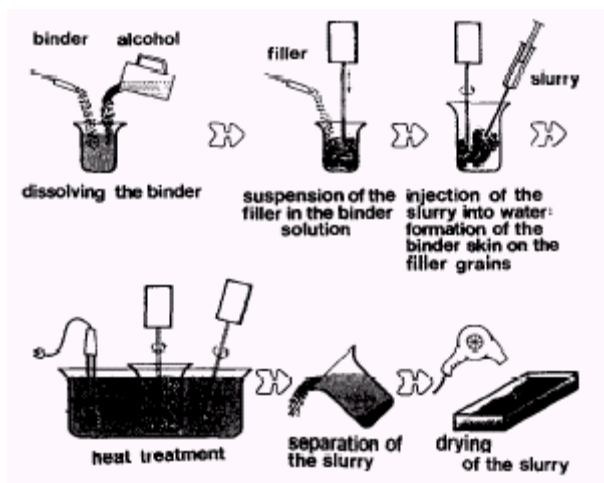


Fig15: Outline of the Coat-Mix process

Base-acid process.

Novolak resins are soluble in alkali solutions, producing a salt. The subsequent precipitation of the binder takes place by feeding the resultant aqueous slush into a dilute acid. The precipitation of the binder results from the substitution of the weaker phenolic acid by a stronger acid. Figure 2 shows the equations of the reactions if soda lye is the solvent and hydrochloric acid the precipitation liquid.

The advantage of this procedure is the avoidance of organic solvents. After the mixing process the liquid of the resulting slurry comprises water, acid and dissolved NaCl. The hydrochloric acid is neutralized by sodium hydroxide. This procedure has been used in the production of carbon fillers.

Compared with the normally used mixing processes, the “base-acid process” offers some advantages. For example, there is the possibility of making the mixing step a continuous process. Moreover, it is conceivable that the synthesis of the binder and the mixing of filler and binder could be combined into one continuous procedure. Of course, the procedure has not yet been realized on an industrial scale. A disadvantage of the process may be the salinity of the waste water.

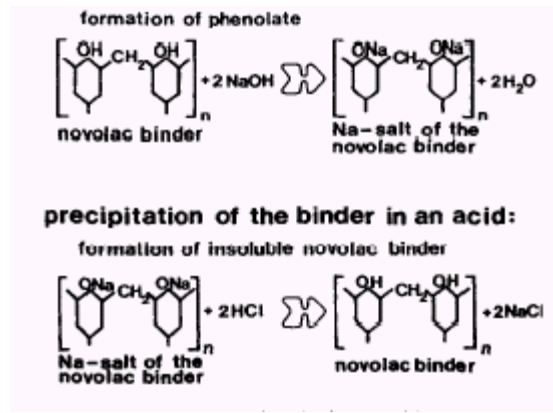


Fig 16: Reactions for the base-acid process

Thermal treatment

After the mixing step the filtration of the resulting slurry is difficult, because the coated filler grains and the liquid form a curd-like mass in both the “solvent” and the “base-acid” processes. However, by warming up the slush under agitation to a temperature lower than the boiling point of the solvent it is possible to obtain a suspension that can be easily filtered. It seems that during this step residues of solvent and water are removed from the binder coatings, which shrink onto the surface, fitting the filler grain surfaces without forming pores. The obtained suspension can be filtered like sand.

Decantation, filtration and drying

After thermal treatment the slurry is cooled down, decanted and filtered. The filter cake is washed with water to remove residual solvent, or dissolved NaCl and remaining HCl in the case of the base-acid process. After washing, the filter cake has a water content of about 30-40 mass%. The wet mass of coated filler particles is then dried without any mechanical treatment. Initially, the drying of the slush caused difficulties. The moist binder coatings of the filler particles are very sensitive to mechanical interferences during drying, caused by, for example, stirring, rotations or other mechanical movements. Hard conglomerations are formed very easily. To avoid this difficulty a drying method called “vacuum condensation drying” was developed. By this method it is possible to dry CM powders with water contents less than 1 mass% at low

temperatures. Compared to other drying methods this process works economically, is energy saving and is environmentally benign.

After drying, any agglomerations formed can be crushed or milled very easily. The CM process is especially advantageous for the mixing of fine grain fillers with binder. The maximum allowable grain size is in the range of 1 mm. The minimum seems to be very low, because it has proved possible to coat even very small soot particles (up to 50 nm).

6.2.1 Direct-mix technique

After dissolving the binder in a minimum amount of alcohol, the filler powder (synthetic graphite) is added to get the paste. The paste is then dried to remove the solvent, the first in partial vacuum and then in air. The resulting sample is then powdered and molded.

6.3 Molding techniques:

6.3.1 Hot molding technique:

3gm of pulverized sample is taken in the die and is then placed on the bottom plate of the molding press. The top plate is then lowered until it just touches the surface of the die. After that, the heating is started until a final temperature of 150°C is reached. As the molding temperature is attained, a load of 20 kg/cm² is applied. The system is then left under these conditions for 30 minutes. After that, the heating is stopped and the cooling of die is done in air without the removal of load. As the die reaches a temperature of around 60-70°C, the molded plate is removed and characterized.

6.3.2 Cold molding technique:

3gm of pulverized sample is taken in the die and is then placed on the bottom plate of the molding press. The top plate is then lowered and a load of 20 kg/cm² is applied. The molding is done at room temperature. The load is applied for 8 minutes. The mold is then removed and characterized.

The characteristics of developed through coat-mix method and direct mix methods are given below:

Plates from Coat mix

Table 12: Measurements of Green plates (hot -molded)

Sample No.	Material	Length (cm)	Width (cm)	Thickness (cm)	Volume (cm ³)	Mass (gm)	Density (gm/cm ³)	Electrical Resistivity (mΩ.cm)
1	30% Phenol-formaldehyde & 70% SG in alcohol	5.032	1.2179	0.2379	1.458	2.818	1.933	24.0
2	20% Phenol-formaldehyde & 80% SG in alcohol	5.031	1.2177	0.2477	1.518	2.835	1.868	10.3

Table 13: Measurements of 1000°C treated Plates (hot -molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Volume (cm ³)	Mass (gm)	Density (gm/cm ³)	Electrical Resistivity (mΩ.cm)
1	4.962	1.2010	0.2358	1.405	2.6592	1.892	1.09
2	5.010	1.2150	0.254	1.540	2.737	1.780	1.09

Table 14: Measurements of 1400°C plates (hot -molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm ³)	Electrical Resistivity (mΩ.cm)	Bending strength (MPa)	Modulus (GPa)	Shore Hardness
1	4.962	1.2026	0.237	2.655	1.870	0.93	57.56	15.06	60
2	5.009	1.2132	0.254	2.733	1.770	1.04	41.23	6.42	65

Table 15: Measurements of Green plates (cold -molded)

Sample No.	Material	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	30% Phenol-formaldehyde & 70% SG in alcohol	4.022	1.0058	0.4366	3.0233	1.7126	63.81

Table 16: Measurements of 1000°C treated Plates (cold Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	3.9863	0.9956	0.4284	2.8734	1.696	1.57

Table 17: Measurements of 1400°C treated plates (cold Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)	Bending strength (MPa)	Modulus (GPa)	Shore Hardness
1	3.986	0.9963	0.428	2.8685	1.69	1.30	32.76	6.934	55

Plates from Direct-mix method

Table 18: Measurements of Green plates (Hot Molded)

Sample No.	Material	Length (cm)	Width (cm)	Thickness (cm)	Volume (cm³)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	30% Phenol-formaldehyde & 70% SG in alcohol	2.691	1.214	0.2577	0.842	1.649	1.959	9.71

Table 19: Measurements of 1000°C treated Plates (Hot Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Volume (cm³)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	2.651	1.195	0.2561	0.842	1.543	1.902	1.08

Table 20: Measurements of 1400°C plates (Hot Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)	Bending strength (MPa)	Modulus (GPa)	Shore Hardness
1	2.651	1.1956	0.2582	2.263	1.88	0.94	49.8	9.94	67

Table 21: Measurements of Green plates (Cold Molded)

Sample No.	Material	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	30% Phenol-formaldehyde & 70% SG in alcohol	3.8485	1.025	0.462	2.701	1.48	49.47

Table 22: Measurements of 1000°C treated Plates (Cold Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)
1	3.775	1.01	0.452	2.538	1.47	3.03

Table 23: Measurements of 1400°C plates (Cold Molded)

Sample No.	Length (cm)	Width (cm)	Thickness (cm)	Mass (gm)	Density (gm/cm³)	Electrical Resistivity (mΩ.cm)	Bending strength (MPa)	Modulus (GPa)	Shore Hardness
1	3.330	1.01	0.45	2.26	1.47	2.74	21.76	2.45	43

Chapter 7: Applications of Glass-Like Carbon

7.1. Introduction

It has already been shown earlier that glass-like carbon is an engineering material as it combines some of the properties of glass such as lustre, mode of fracture and imperviousness with those of normal industrial carbons. Its chief characteristics such as high strength and hardness, high resistance to corrosion and erosion, low porosity and permeability make glass-like carbon a versatile material in a wide range of analytical, metallurgical, mechanical, electrical, electronics and biomedical applications. Further, it has also been mentioned that the manufacturing technology of this form of carbon has been kept highly secretive and consequently there are only a few firms in the world. It has been shown that glass-like carbons can be developed by the controlled carbonization up to a temperature of 950°C or higher of a suitable phenol formaldehyde resin precursor. The characteristics of glass-like carbons made in the present investigations have been found to compare well with those available commercially. The present chapter describes the development and applications of glass-like carbon in biomedical, semiconductor, analytical and other specialized fields. It has been demonstrated over the past two decades that carbon in all its forms including the glass-like form is uniquely biocompatible with living tissues and is now universally accepted by the surgeons for implantation in the body. Several publications point out the use of glass-like carbon or vitreous carbon for heart valve, dental implants and percutaneous connections in the body.

Glassy carbon artifacts find numerous applications in the form of crucibles, beakers and other vessels, components of ovens etc., suitable for elevated temperatures and harsh environments (zone melting, monocrystals preparation, decomposition by acids, hydroxides). Tip electrodes for pacemakers, some bone substitution, artificial tooth roots, and special plates for cultivation of microbes. Important utilization is in analytical electrochemistry.

7.2 Glass-Like Carbon Artifacts for Analytical Applications

7.2.1. Glass-Like Carbon Crucibles for Silicon Processing

Besides the use of glass-like carbon dental implants, efforts are made to use glass-like carbon crucibles in silicon processing application for solar energy utilization. Solar grade silicon is melted in special graphite crucibles at 1450° C and allowed to recrystallize in the process of cooling it. The graphite crucibles have to be of certain strict specifications in respect of density, strength, thermal expansion and purity. Such graphite crucibles are not commercially produced in the country and have to be imported at premium prices.

The crucibles are used for melting and crystallization of solar grade silicon. It has been found that these crucibles work successfully without any breakage which usually occurs during the solidification of molten silicon. It can be concluded from the present investigations that glass-like carbon crucibles can serve well in silicon processing for solar energy utilization.

7.2.2. Glassy Carbon Resistor Plates and Crucibles for Thin Film

Applications

Glass-like carbon artifacts have potential applications in the field of thin films, where this material can be used either as resistor plates of high current capacity or as crucibles. The test material is taken on the resistor plate or in the crucible and is made to evaporate under conditions of high temperature and high vacuum to result in the deposition of thin films on suitable substrates.

Test tubes made from glassy carbon are universally used in laboratories worldwide for carrying out chemical analyses and also for the preparation of fluorophosphate and other glassy materials. Test tubes fabricated in glassy carbon are also used in the growing of single crystals and other ultra-high purity materials. Tubes



Fig 17: Various artifacts made from Glass-like Carbon

and other shapes fabricated from glassy carbon are used for the zone refining of metals[32].

72.3 Glass-Like Carbon Electrodes

Electrodes can be easily fabricated from oligomers by formation of a thin film on conventional glassy carbon followed by thermal treatment, or by compressing the materials in powder form into 1-cm diameter pellets followed by thermal treatment to form doped glassy carbon. The electrodes fabricated by these techniques function as practical electrodes. Method of preparation allows for the preparation of novel electrodes in which precious metal particles are dispersed within the carbon matrices.

Biochemical Sensors

DNA deposited on nano-sized Au assembled on a glass carbon electrode by an electrodeposition process. This modified electrode can selectively determine uric acid and norepinephrine in the presence of a larger amount of ascorbic acid[33].

For Quantitative Analysis of drugs - electrochemically pretreated glassy carbon electrode is used e.g. for Azithromycin in Pharmaceuticals [34]

Inert Redox Electrodes

for electrometric redox titration, potentiometric or voltametric electrodes for acidobasic analysis, also in the non-water solvents).Inert carriers of mercury film electrodes.

RVC - Reticulated Vitreous Carbon

Open pore foam material composed solely of vitreous carbon - Porous Electrodes for electrochemical processes that require very high current distribution areas, low electrical or fluid flow resistance, and minimal cell volume loss to electrodes[35].

High Temperature Insulation

for inert gas and vacuum furnaces where its ease of fabrication, self-supporting nature, low density, low outgassing, low heat capacity and excellent K value combine to improve efficiency and reduce costs over conventional insulating materials[35].

Filters and Demisters

for molten metals, corrosive chemicals, high or low temperature gases and liquids, where maximum chemical inertness combined with good filtration and detrainment is needed[35].

Storage Batteries

in high energy density batteries, such as the sodium/sulfur and lithium aluminum/ iron disulfide systems, where its unique "caging" effect on infused materials benefits performance, reduces cost[35].

Pt-HGC as a Fuel Cell Cathode

A catalyst was prepared by dispersion of the polymer precursor Hetero-atom doped glassy carbon (HGC) on high surface area carbon, followed by thermolysis under controlled conditions. The so-obtained black powder was then dispensed in a Nafion® and glycerol solution to yield an ink, which was then applied to the polymeric membrane. The electrochemical cell is then assembled according to Fig. 6.3. A gas diffusion backing carbon cloth is sandwiched between each electrode and graphite block in order to allow even diffusion of the gases on the catalytic films .It is also being used in Fuel cells as separator and electrode base[36].

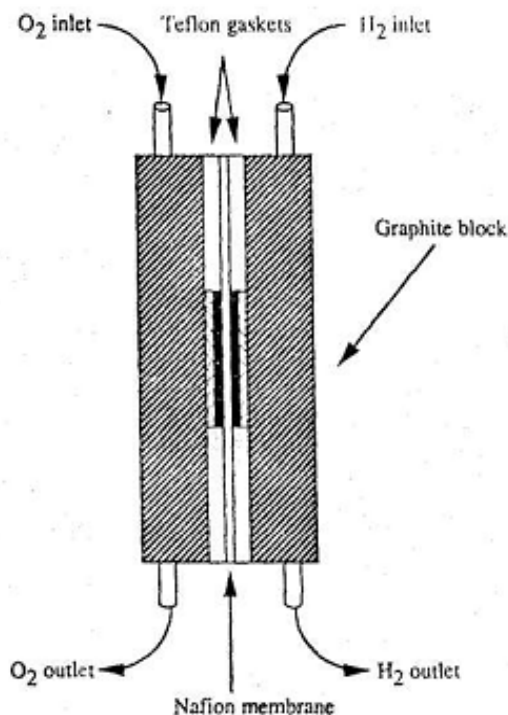


Fig 18: Fuel Cell Assembly

Microcrystalline Platinum Doped Glassy Carbon

A electrode designed to incorporate platinum in glassy carbon involved the dispersion of commercially available Platinum (IV) oxide in the parent carrier polymer. Poly(phenylene diacetylene) was mixed with 0.25 and 1 atom % of platinum(IV) oxide. The intimate mixture was then pressed and thermally treated to 600 °C to form pellets of glassy carbon. These platinum HGC electrodes exhibited excellent stability and no evidence of degradation was found after several thousand reduction cycles. However, overpotential of 50-100 mV, in comparison with a bulk platinum electrode, was found for the reduction[37].

6.2.5 Semi-Conductor Manufacture

Glass-like carbon offers unique advantages in etching and diffusion treatment carriers, reduces manufacturing cost[35].

6.2.6 Acoustic Control

A specially densified form combines outstanding high temperature resistance in non oxidizing environments with excellent noise absorption in the 250 Hz to 3 kHz range[35].

6.2.7 Reference Material for Thermal Expansion of Solids

Glass-like carbon is a candidate reference material for thermal expansion of solids, in particular, at high temperatures[38].

Chapter 8: Result and Discussion

Developments in the field of glassy carbon and its applications have been reviewed. Phenol formaldehyde and Resorcinol formaldehyde resins have been used to synthesize glass like carbon. Characterization of glassy carbon by studying various properties like green density, bulk density, volume shrinkage, transverse breaking strength, electrical resistivity and SEM have been studied. The results of various property measurements show consistency with the established literature and are comparable to that of commercially available glassy carbon.

Glass like carbon synthesized from Phenol formaldehyde resins has better mechanical and barrier properties than those from Resorcinol formaldehyde and hence is used as binder in preparation of bipolar plates.

Characterization of bipolar plates by studying various properties like green density, bulk density, transverse breaking strength, electrical resistivity and shore hardness have been studied.

The better mechanical and electrical properties of bipolar plates prepared by Coat-mix technique is due to uniform distribution along with better binding of filler material.

Chapter 9: Conclusion

1. The glassy carbon, can be fashioned into multitudinous forms which are universally used in semiconductor, electronic, biomedical, analytical and other specialized fields namely thin film deposition and other industries Its hardness is close to that of diamond but its appearance (e.g. black) is reminiscent of graphite and has crack propagation, glass-like lusture and impermeability of glass. High thermal conductivity, no adhesion of noble metal melts, longer service life than graphite crucibles, resistance to thermal shock make it excellent replacement for graphite, metal electrodes. Other then cost of manufacturing there is no reason to limit use of glass-like carbon.
2. It is also evident from the observations that the cold molded bipolar plates lead to lower mechanical and electrical properties as compared to hot molded plates. Thereby showing the hot molding is necessary to get better properties.
3. The composition of the properties of the samples develop through the coat-mix is better method as compared to Direct mix technique.

References

- [1] <http://www.plasticindustry.org/>
- [2] <http://en.wikipedia.org/>
- [3] K. Kamide and Y. Miyakawa, Makromol. Chem. 179. 359 (1978)
- [4] <http://www.chemicaland21.com/>
- [5] Hydrocarbon Process. 90 (mar. 1976); 216 (Nov. 1965); 183 (Nov. 1969); 150 (Nov. 1975); 135 (Nov. 1973)
- [6] S.YAMADA and H. SATO, Nature 193 (1962) 261.
- [7] H.W. DAVIDSON, Nucl. Eng. 7 (1962) 159.
- [8] S. Yamada, H. Sato and T. Ishii, Carbon 2 (1964) 53.
- [9] J.C. Lewis, B. Redfern and F. C. Cowlard, Solid State Electron. 6 (1963) 251.
- [10] F.C. Cowlard and J.C. Lewis, J.Mater.Sci. (1967) 507
- [11] British Patent 889351 (1962)
- [12] British Patent 956452 (1964)
- [13] British Patent 1020441 (1966)
- [14] British Patent 1266685 (1972)
- [15] British Patent 620381
- [16] British Patent 1228910 (1968)
- [17] British Patent 1033277 (1966)
- [18] T. Ishikawa, H. Teranishi and H. Honda, Paper presented at 8th Carbon Conference, June 1967, Buffalo, USA
- [19] W. Bradshaw, P. Pinoli, G. Watsey and H. Wington, paper presented at 8th Carbon Conference, June 1967, Buffalo, USA.
- [20] S. Yamada, DCIC report 68-2, April 1968 Battled Memorial Institute, Ohio, USA.
- [21] D.W. McKEE, Ann. Rev. Mater. Sci. 3 (1973) 195.
- [22] G.M. Jenkins and K. Kawamura, "Polymeric Carbons – Carbon Fibre, Glass and Char" (Cambridge University Press, Cambridge, 1976)
- [23] G.M. Jenkins and C.J. Grigson, J. Biomed. Mater. Res. 13 (1979) 371
- [24] W. Mitchell Jr., et al., Academic press, New York, 1963.

- [25] J. Moriera, A.L. Ocampo, P.J. Sebastian, M.A. Smit, M.D.Salazaar, P.del Angel, J.A.Montoya, R.Perez and L.Martinez, *Int J Hydrogen Energy* 28 (2003), PP. 625-627.
- [26] F. J. Dias, H. K. Luhleich, H. Nickel and P. Pflaum, *Extended Abstracts. "Carbon 82", VIth London International conference on carbon and Graphite*. London, p. 4 (1982).
- [27] Mantell, Handhook (*!f Carbon und Graphite*, Wiley. New York (1968).
- [28] K. Bach. J. Dias, P. Glozbach, M. Kampel, H. K. Luhleich and P. Pflaum, *Extended Abstracts. "Carbon '82" VIth London International Conference on Carbon and Graphite*, London, p. 16 (1982).
- [29] H. Luhleich. H. Nickel. P. Pflaum and F. Dias, US Patent No. 4023979 (1975).
- [30] F. J. Dias and H. Luhleich, LJS Patent No. 4221689 (1978).
- [31] F. J. Dias, W. Hannen, H. Luhleich and P. Pflaum, US Patent No. 4347671(1984).
- [32] <https://secure.2spi.com/spihome.html>
- [33] Liping LU and Xiangqin LIN, *Analytical Sciences* March 2004, Vol. 20, 527
- [34] Biljana Nigovic, *Analytical Sciences* April 2004, Vol. 20, 639
- [35] Wilson, M.S.; Gottesfeld, S.J. *Appl. Electrochem.* 1992
- [36] Thomas X. Neenan, AT&T Bell Laboratories, Matthew R. Callstrom, Department of Chemistry, Ohio State University, Review on Glassy Carbon.
- [37] Reticulated Vitreous Carbon, Materials and Aerospace Corporation, 900, Stanford Avenue Oakland, CA
- [38] H. Watanabe, N. Yamada, N. Okaji, Linear Thermal Expansion of Candidate Reference Materials; Glass-like Carbon