Chapter I

Introduction

I.1 Introduction

The term carbon foam has been used for designing feebly composed exfoliated graphite earlier. [1] Now carbon foam means a carbonaceous porous solid having well connected network of struts. Many modern day natural occurring porous materials are being used for a long time, e.g. wood, cork, bone, etc. in many applications in day to day life by human beings. Having derived inspiration from nature, several synthetic cellular materials have been developed, e.g. polymeric foams for packaging, metallic in crush protection and ceramic for water purification. [2]

I.2 Types of foam

With specific application of foam, foam of any material or composition are being developed e.g. polymeric foam for room to low temperature applications, metallic foam for structural applications and ceramic foam for high temperature insulation applications etc. with all structural ligaments or struts interconnected as well as open cell porosity interconnected enabling fluid to pass freely into and out of foam structure or foam with closed pores isolated from each other. The foams can be classified into two types based on their pore structure: open cell structured foams (also known as reticulated foams i.e. like a net) and closed cell foams shown in figure I.1.

![Figure I.1: open cell foam (A) and closed cell foam (B) [3,4]](image-url)
Open cell structured foams are relatively soft as they contain pores that are connected to each other and form an interconnected network. Open cell foams can be filled with whatever those are surrounded with. If filled with air this could be a relatively good insulator, but if the open cells are filled with water, insulation properties would be reduced. The solid component of reticulated foam may be an organic polymer like polyurethane, a ceramic or a metal. These foams are used in wide range of applications where high porosity and large surface area are needed, including filters, catalyst supports, fuel tank inserts, and loudspeaker covers.

Closed cell foams have isolated pores. Normally closed cell foams have higher compressive strength due to their structures. However, closed cell foams are also generally denser, require more material, and consequently are more expensive to produce. The closed cells can be filled with a specialized gas to provide improved insulation. The closed cell structure foams have higher dimensional stability, low moisture absorption coefficients and higher strength compared to open cell structured foams. All types of foam are widely used as core material in sandwich structured composite materials. The disadvantage of the closed-cell foam is that it is denser, requiring more material, and therefore, more expensive.

I.3 Basic terminologies of foams

I.3.1 Strut, cell and pore

The microstructure of foam in figure I.2 shows cells, pores and struts. The basic structure of foam is made up of interconnected cells. The cells are made of pores and connected through struts. Struts are also called ligaments. In given foam, there are pores joined through ligaments. The volume occupancy of highly porous structure is shown in figure I.3.
The unit cell in foam resembles a polyhedron with pentagonal or hexagonal faces that limit a spherical-like inner space. Each cell, defined by hollow volume of the polyhedron, constitutes a pore. The cell size is commonly expressed in terms of pores per linear inch (PPI): the overall range of variation in cell size goes from 5 PPI to 100 PPI (figure I.4). [6] Typical porosity values range from 80 % to 97 %.

**Figure I.2:** Microstructure of foam

**Figure I.3:** Volume share of highly porous structure [5]

**I.3.2 Classification based on PPI value**

The unit cell in foam resembles a polyhedron with pentagonal or hexagonal faces that limit a spherical-like inner space. Each cell, defined by hollow volume of the polyhedron, constitutes a pore. The cell size is commonly expressed in terms of pores per linear inch (PPI): the overall range of variation in cell size goes from 5 PPI to 100 PPI (figure I.4). [6] Typical porosity values range from 80 % to 97 %.
I.3.3 Relative Density of foam

Relative density is the density of foam divided by the density of the solid parent material of the struts. In other words, it is the mass of real material in a block of foam compared to what it would be if it were a solid block of the same material. Typical relative densities for foams range from about 2% to 15% depending on the material being foamed and the application. The relative density varied with the shape and size of struts. Different types of structures are given in figure I.5.

![Relative Density Diagram](image)

Figure I.5: Change in relative density with ligament Cross Sections

While pore size controls number and nominal size of foam ligaments, the relative density controls the ligament cross-section shape and actual size. Since foams can be compared to miniature three-dimensional strut structures, it is apparent that the cross section and moment of inertia of the struts or ligaments is a primary driver of foam mechanical properties like stiffness, rush strength, electrical conductivity, and thermal conductivity [6]

I.3.4 Structure of open cell foam

Synthetic cellular materials such as open-cell foams have a complex microstructure consisting of an interconnected network of ligaments that form along the edges of randomly packed cells that evolve during foaming process. The cells are irregular polyhedra with anywhere from 9 to 17 faces when the foam is nearly monodisperse (figure I.6). The material is concentrated in the nearly straight edges of the polyhedra and in the nodes where they intersect, usually four at a time (figure I.7 and I.8). The design and use of foams require that the microstructure be related to the properties (mechanical, thermal, acoustical, etc.). [7]
Figure I.6: Computed tomography image of a 20-ppi polyester urethane foam 

\( \frac{\rho^*}{\rho} = 2.36\% \).

Figure I.7: (a) Cells extracted from 3-ppi polymeric foam illustrating irregular polyhedral geometry. Polyhedra are somewhat elongated in rise direction. (b) Skeletal drawing of the cells in (a).

They then used this information to generate model foams based on the 14-sided cell of Kelvin. It was shown that geometric characteristics such as material distribution in ligaments and nodes, and cell anisotropy play a decisive role in the mechanical behaviour of the foams. These characteristics are essential for quantitatively accurate predictions of all mechanical properties. [14,15]

Figure I.6 shows a 3D image consisting of a few cells from a 20-ppi foam (vertical corresponds to the rise direction). The cells are seen to be irregular polyhedra with nearly straight edges (ligaments) that have the characteristic three-cusp hypocycloid cross section of Plateau borders. The foaming process results in some elongation of the cells in the rise direction that is apparent in the figure. The polyhedral geometry of cells is illustrated in figure I.7(a), which shows two individual cells extracted from the coarsest foam. Figure I.7(b) shows a skeletal outline of the cells formed by joining the centres of adjacent nodes with straight lines. The one on the LHS has 14 faces that include 3 quadrilaterals, 8 pentagons, 3 hexagons and a total of 35 ligaments. The one on the RHS has 17 faces with 3 quadrilaterals, 7 pentagons, 6 hexagons, 1 heptagon and a total of 45 ligaments. Although four ligaments commonly join at a node, higher connectivity is also possible. For example the node circled in figure I.7(b) has a connectivity of 6. [15]

Figure I.8 shows two ligaments of different length extracted from the 3-ppi foam. Figure I.8 shows that the cross sectional area of the ligaments changes along the length. GKJ conducted a limited number of measurements of the area distribution and demonstrated that this is an important parameter for mechanical properties.
Chapter I

Figure I.8: Ligaments from 3-ppi foam and cross sectional views: (a) \( \ell \approx 4.2 \text{ mm} \) and

(b) \( \ell \approx 2.1 \text{ mm} \)

Figure I.9: Images showing three four-ligament nodes from 3-ppi foam

The nodes are zones of material concentration that must be accounted for. Figure I.9 shows images of three isolated nodes from the 3-ppi foam. They are all junctions of four ligaments, which is by far the most commonly occurring type. The nodes are seen to have smooth curved surfaces while simultaneously they are significant concentrations of material.

I.4 Classification of foams according to their raw materials

The solid component of foam may be an organic polymer like polyurethane, a ceramic or a metal. Figure I.10 shows examples of different types of foams according to their raw materials.
I.4.1 Polymeric foams:

Polymer foams are made up of a solid and gas phase mixed together to form a foam. Polymer foams can be divided into either thermoplastics or thermosets, which are further divided into rigid or flexible foams. Examples of different polymeric foams are given in figure I.11. Polymer foams are found virtually everywhere in our modern world and are used in a wide variety of applications such as disposable packaging of fast-food, the cushioning of furniture and insulation material.

I.4.2 Metallic foams:

Metal foams are a new class of material, as yet imperfectly characterised, but with alluring properties. They are light and stiff, they have good energy-absorbing characteristics (making them good for crash-protection and packaging) and they have attractive heat-transfer
properties (used to cool electronic equipment and as heat exchangers in engines). Figure I.12 shows examples of metallic foams such as copper, silicon, gold and titanium foam.

Figure I.12: (i) Copper foam, (ii) silicon foam, (iii) gold foam and (iv) titanium foam [19]

I.4.3 Ceramic Foams:

Ceramic foam is usually manufactured by impregnating open-cell polymer foams internally with ceramic slurry and then firing in a kiln, leaving only ceramic material. The foams may consist of several ceramic materials such as aluminium oxide. The foam is often used for thermal insulation, acoustic insulation, adsorption of environmental pollutants, filtration of molten metal alloys and as substrate for catalysts requiring large internal surface area. It has also been used as stiff lightweight structural material, specifically for support of reflecting telescope mirrors. Ceramic foams like zirconia (ZrO$_2$), silicon carbide (SiC), alumina foam (Al$_2$O$_3$) and carbon foam are shown in figure I.13.

Figure I.13: (i) Zirconia foam, [20] (ii) silicon carbide foam, [20] (iii) alumina foam [20] and (iv) carbon foam [6]
I.4.4 Comparative properties of different foams:

Cellular solids - ceramics, polymers, metals - have properties that depend on both topology and material. Performance and properties depend naturally on the macro- and microstructure of the cellular ceramic component: the presence of cell walls influences both permeability and strength, while compositional purity affects chemical and oxidation resistance, as well as high-temperature creep, electrical resistivity and thermal properties.

Density of ceramic foams is lower than that of metal foam. Ceramic foams offer very high wear resistance, corrosion resistance and thermal stability as compared to metallic and polymeric foams. Electrical and thermal conductivity of ceramic foam can be manipulated by selecting appropriate raw materials. Both insulator and good conductor of thermal and electrical can be prepared. The physical properties like hardness and elastic modulus is very high as compared to metallic and polymeric foams.

Three possible stress dominated collapse mechanisms of foams studied by Gibson & Ashby are given in figure I.14. [8] The elastomeric foams (rubbers) collapse is accompanied by the elastic buckling of cell walls, in materials with a plastic yield point (metals) it occurs by the formation of plastic hinges at the maximum load and in brittle material such as ceramics it was caused by brittle fracture of the struts [21].

**Figure I.14:** (A) Foams made of ductile materials collapse by the plastic bending of the cell edges, (B) A brittle foam collapses by the successive fracturing of the cell edges. Ceramic
foams generally show this collapse mechanism and (C) An elastomeric foam collapses by the elastic buckling of the cell edges

1.5. Porous ceramics and its development:

Macroporous ceramics with pore sizes from 400 nm to 4 mm and porosity within the range 20 % – 97 % have been produced for a number of well-established and emerging applications, such as molten metal filtration, catalysis, refractory insulation, and hot gas filtration. [22] The numbers of applications that require porous ceramics structure have largely increased in the last decades, especially for environments where high temperatures, extensive wear and corrosive media are involved. [23–25] The advantages of using porous ceramics in these applications are usually high melting point, tailored electronic properties, high corrosion, and wear resistance. 

Keeping this in view a thorough literature survey was carried out on processing routes of carbon and ceramic foams.

1.5.1. Outline of various routes to fabricate the porous ceramics

The main fabrication techniques for preparation of ceramic foam such as honeycomb structures and interconnected rods, fibres and hollow spheres were reviewed by Colombo. [26] The fabrication and use of cellular ceramics in a vast number of different fields has also been described in a recent book edited by Scheffler and Colombo. [27] While this valuable literature contains extensive information on the production and applications of cellular ceramics, the processing– microstructure–property relations for each of the main processing routes has not been fully explored.

The processing routes described have been classified into replica, direct foaming methods and sacrificial template, as schematically illustrated in figure I.15 (A, B & C). The techniques differ greatly in terms of processing features and final microstructures/properties achieved. The processing features of each of these methods are thoroughly discussed and
compared with regards to the versatility and ease of fabrication, as well as their influence on the microstructure and mechanical strength of the final macroporous ceramics.

**Figure I.15:** (A) Replication of sacrificial foam template, (B) Direct foaming of liquid slurry and (C) Sacrificial template method

1.5.2. Replica Technique

Early 1960s, Schwaetwalder and Somers [1] started using polymeric sponge as template to prepare ceramic cellular structures of various pore size, porosities and chemical compositions. After that sponge technique has become most popular method to produce
macroporous ceramics and due to simplicity and flexibility of this method, it is widely used in industry to prepare ceramic filters and other applications. In this method ceramic suspension or precursor solution that contain ceramic is impregnated in cellular structure and after sintering it turns into a macroporous ceramic exhibiting replica of original porous material. Figure I.15(A) shows schematic of sacrificial replica foam method.

The polymer foam (i.e. template) is usually made of polyurethane, but other polymers such as polyvinyl chloride, polystyrene, cellulose, phenolic, latex, etc. have been tested successfully as well. The organic foam used must contain properties like ability to regain its shape after squeezing or passing from rollers, adhesion between ceramic suspension and template, and complete and clean burn out during sintering. The ceramic slurry can be of wide variety of oxides or non-oxides which contains various modifiers like binder (aluminium orthophosphate, potassium and sodium silicates, magnesium orthoborate, colloidal silica, hydrated alumina), plasticizers (polyvinyl butyral with polyethylene glycol), antifoaming agents, setting compounds, rheological agents, etc. [28-31]

The crucial step is the coating process, incomplete removal of ceramic slurry end up with some blocked pores in ceramic foam which alter mechanical properties and permeability behaviour. To prevent cracks, defect and collapse of ceramic foam the heating rate must be well controlled (slow) during sintering. When coating is performed on polymeric foam, it swells up to certain extent. But when sintering is carried out it again shrink due to removal of polymeric template, volatiles, additives, etc. that can damage the ceramic coating, if not carefully controlled. Only open cell ceramic foams having cell size ranges from approximately 100 µm to few millimetres can be prepared using this route depending upon the polymer template used. Relative density typically varies between 5 to 30 % theoretically. Cichocki et al. [32] synthesized graded porous structures having cell size varies along one
axis can be obtained either by stacking templates with different morphological features or by compressing a wedge-shaped polymeric template.

Using CVD (chemical vapour deposition), CVI (chemical vapour infiltration) and sol-gel coating of various oxide, nitride, boride, silicide, carbide, metals etc. on polymeric template, the ceramic composite foam having controlled thickness can be obtained. [33] The density, porosity, mechanical properties, strut thickness, chemical composition, etc. can also be manipulated using multiple infiltration cycles.

1.5.3. Natural Templates

In addition to synthetic polymer foams, other cellular structures had been used as templates for fabrication of macroporous ceramics through replica approach. Biomimetic approach used in the “replamine form” technique, many investigators have studied transformation of wood cellular structures into macroporous ceramics (figure I.16).

![Processing routes to transform cellular wood structures into macroporous ceramics](image)

**Figure I.16:** Processing routes to transform cellular wood structures into macroporous ceramics [34]

The most common approach was to first prepare a carbon cellular preform by heat treating wood structure under inert atmosphere at temperatures within 600 –1800 °C. The porosity of these structures was predominantly open and can vary from 25% up to 95 % depending on the amount of material impregnated into the template.
The anisotropic nature of cellular ceramics produced using wood as template might be very advantageous in applications that require open and highly oriented porous structures, such as in catalysis and in the filtration of liquids and hot gases. [34] The disadvantage of the wood-replica approach is the several time-consuming steps involved, which might add considerable costs to the process.

1.5.4. Direct foaming of liquid slurry

Direct foaming consists in generation of bubbles inside liquid slurry containing ceramic powders or inside a ceramic precursor solution to create foam which then needs to be set without collapsing obtained porous network before heating to high temperature. (figure I.15(B)) The foaming agent can be a volatile liquid (low boiling point solvents) or solid (CaCO$_3$ powder which decompose on heating), or gas can be developed in situ by chemical reactions (oxidation of solid C or SiC filler forming CO$_2$ gas) or can be added to the liquid mixture by mechanical stirring or bubbling (gas injection). The total porosity of directly foamed ceramics is proportional to the amount of gas incorporated into suspension or liquid medium during the foaming process. The pore size and interconnectivity, on the other hand, is determined by the stability of the wet foam before setting takes place. In order to avoid collapsing of liquid foam and to sustain its porous network, special additives need to be added to liquid in order to cure foamed structure once it is stabilized. [22]

1.5.5. Sacrificial template method

The sacrificial template technique usually consists of the preparation of a biphasic composite comprising a continuous matrix of ceramic particles or ceramic precursors and dispersed pore former phase that was initially homogeneously distributed throughout matrix and was ultimately extracted to generate pores within the material. The schematic diagram of burn-out pore former fugitive method is shown in figure I.15(C).
A wide variety of materials had been used as pore formers, including compound of natural and synthetic organics, liquids, ceramics, metals, polymers, proteins, etc. which decompose or degrade or dissolve leaving behind the porous structure depending upon pore former used and removal method.

Porous ceramics obtained with the sponge replica method can give open porosity within the range 40%–95% and was characterized by a reticulated structure of highly interconnected pores with sizes between 200 mm and 3 mm, as outlined in figure I.17.

![Figure I.17: Typical porosity and average pore size achieved via the replica, sacrificial templating, and direct foaming processing routes.](image)

The high pore interconnectivity enhances permeability of fluids and gases through porous structure, [35] making these reticulated materials very suitable for high throughput filtration.

A disadvantage of sponge replica technique is that struts of reticulated structure are often get cracked during pyrolysis of the polymeric template, which drastically decreases final mechanical strength of the porous ceramic. [36] Figure I.18 shows that strut flaws reduce compressive strength of replica-derived porous ceramics to levels usually lower than strength theoretically predicted for open cell structures. [37]
Figure I.17: Relative compressive strength as a function of the relative density of macroporous ceramics produced via replica, sacrificial template and direct foaming methods.

By controlling foam stability and setting kinetics, pore sizes within the range of 35 mm to 1.2 mm have been achieved using above surfactant-based direct foaming methods (figure I.17). It also shows that the porosity of cellular structures produced via surfactant-based direct foaming can be tuned from approximately 40% up to 97%. The pores obtained with this method are typically spherical and can be either closed or opened depending on the foam wet processing.

All method discussed above viz. replica method or direct foaming method or burn-out of fugitive pore former offers possibility to develop ceramic foams with wide range of morphology and properties. Selection of processing technique basically depends on type of application aimed and thus microstructural characteristics. Porous ceramics obtained with the sponge replica method can gives open porosity within the range 40%–95% and was characterized by a reticulated structure of highly interconnected pores with sizes between 200 mm and 3 mm, as outlined in figure I.17. Replication technique is a well established method.
to prepare ceramic foams in the range of 100 micron to 3 mm or more. Direct foaming method yield porous ceramic foam with pore size in range of 10 micron to 1.2 mm. Incorporation of pore former fugitive method produce ceramic foams with pore size in the range of 1 to 100 micron. All the methods differ greatly in terms of processing parameters and final porous ceramic structure obtained. [38]

I.6 Carbon foam

I.6.1 Introduction

Reticulated vitreous carbon (RVC) foam is made up of glassy carbon with a high void volume (up to 97%). [39] High resistance to combustion, resistance to intercalation by materials that disintegrate graphite, good electrical conductivity and chemical inertness to wide range of acids, bases and organic solvents are some of the special properties of RVC. RVC finds use as porous electrodes, as high temperature insulation [40], as filters [41], in storage batteries [42], as scaffolds [43], in semiconductor manufacture [44] and as field emission cathodes. [45] Densified RVCs find use in acoustic control with noise absorption in the range of 250 Hz to 3 kHz.1

RVC foam was synthesized by carbonizing precursor foams which were impregnated by a thermosetting resin. Open cell polyurethane foams were commonly used as precursors. The impregnating resins used for polyurethane precursor foams were generally phenolic resins, epoxy resins or furfuryl alcohol (thermosetting resins). The carbonization rate of furfuryl alcohol impregnated polyurethane foams was found to be higher than that for foams infused with phenolic and epoxy resins. Addition of small amount of clay into polymer matrices provides significant improvement in a wide variety of properties. [46,47] The most widely used clay in composite synthesis was montmorillonite (MMT). The clay particles had a layered platelet structure, in which platelet thickness was about 1 nm and the lateral
dimensions were up to 1 µm. Montmorillonite clays had been found to be powerful cell openers for polyurethane foam. [48]

Femlab [49] used carbon foam to aid in the design of a novel temperature management system. The passive system consists of a carbon foam block that was filled with a Phase Change Material (PCM) and enclosed in an aluminum box. A PCM is a substance which releases a large amount of energy when undergoing a change of phase (solid-solid or solid-liquid). Technology Assessment and Transfer were developed high thermal conductivity, structurally enhanced carbon foam based on a product created at Oak Ridge National Laboratory and licensed and commercially produced by POCO Graphite of Decatur, Texas. TA&T had developed a process to improve the mechanical properties of the foams, and obtained foam having twice the compressive strength with only a 5% loss in thermal conductivity when compared to the commercially available product.

Pitch-based carbon foams are not new, but the development of high thermal conductivity foams for thermal management applications has yet to be explored. The research reported a novel foaming technique and the evaluation of the foaming characteristics of two mesophase pitches (Mitsubishi ARA24 and Conoco Dry Mesophase). After graphitization to 2800°C, densities of the graphite foams ranged from 0.2 to 0.6 g/cm³, with average pore diameters ranging from 275 µm to 350 µm for the ARA24-derived foams, and from 60 µm to 90 µm for the Conoco-derived foams. The thermal diffusivity measurements were performed revealing that the bulk thermal conductivity varied with density from 40 to 150 W/m·K. The specific thermal conductivities of the graphitized foams were more than six times greater than solid copper. [50]

The carbon foams made up of acidic sucrose solution contain spherical cells of size in the range 450–850 µm and that were interconnected through circular or oval shape windows of size in the range 80–300 µm. The carbon foam samples sintered at 1400 °C showed
compressive strength of 0.89 MPa. Also, a number of new applications such as heat exchangers, acoustic panel, electronic heat sinks, EMI shielding, core material for making sandwich structure, ballistic containment cases and fuel cell humidification were proposed for carbon foams. [51]

Radar absorbing materials (RAMs) are widely applied in order to achieve the objective of stealth for military and civil targets. Carbon foams found their way to act as RAMs, mainly due to their well matched impedance, high durability, light-weight, and effective EM wave absorbing capability. [52] Their characteristic structure and properties can be utilized to overcome some of the shortcomings of existing RAMs. [53]

Andrei G. Chakhovskoi et al. [54] demonstrated RVC as a viable field emission electron source for cathodoluminescent lamps. The high void volume and porous structure of RVC help create a large number of natural emission sites on the surface. Emission centres are formed by the sharp edges of the carbon struts, which result from simple machining of the macroscopic open-pore material. Electron emission has been evaluated in the 10 to 500 μA range, in $10^{-6}$ to $10^{-8}$ Torr vacuum ambient. Extended lifetime tests were carried out for over 5000 h in sealed glass prototype devices utilizing commercial cathodoluminescent phosphors. Brightness levels exceeding 10000 cd/m² were achieved for diode and triode configurations. The low cost of manufacturing, along with chemical and mechanical robustness, make RVC a viable material for electron-beam vacuum device applications such as mercury-free cathodoluminescent light sources.

RVC, a material especially known in scientific, electrochemical application was characterized in the skeletal system and in connective tissue, in order to evaluate its properties with respect to tissue engineering. A variety of different carbon based materials was previously described in ophthalmic [55,56] and bone applications [57,58]. Some were even reached clinical use. [59-62]
The in vivo and in vitro results reported by Martina K. Pec et al. [63] in their work clearly point out the potential of RVC Duocel® (pore size 200-400 μm) foams as constructs for tissue engineering and regenerative applications. Because RVC foams are available within a wide range of pore sizes and offer an unusual porous interconnectivity, they could be easily adapted to the necessities of a variety of bone models and regenerative medical applications. In addition, their favourable properties for cell adhesion could give rise to their application for ex vivo cell expansion and/or tissue engineering and should be an issue for future investigation.

Zhao Xuefei et al. [64] prepared activated carbon foam from phenolic resin synthesized with phenol and formaldehyde under alkali condition. Under the optimum experimental conditions, activated carbon foam with a specific surface area 727.62 m²/g was obtained. Moreover, iodine value and carbon tetrachloride value of activated carbon foam was 1050.28 mg/g and 401.37 mg/g, respectively. The pore size of activated carbon foam was in the range of 3.5 – 5 nm which was determined through the nitrogen adsorption test. In addition, the yield of activated carbon foam was 36.24 %.

Carbon foams were successfully prepared using polyurethane foams as a template by M. Inagaki et al. [65] Polyurethane/ polyimide composite foams prepared by impregnating poly(amide acid) could convert to polyimide foams by heating above 400 °C and then to carbon foams by heating above 650 °C. Graphite foams with relatively high graphitizability were prepared by heat treatment at 3000 °C. Two applications of these carbon foams, i.e., an adsorbent of ambient water vapour and a substrate of photo catalyst anatase TiO₂, were proposed through preliminary experiments.

**I.6.2 Structure of carbon foams**

Atomic carbon is a very short-lived species and, therefore, carbon is stabilized in various multi-atomic structures with different molecular configurations called allotrops. The
three relatively well-known allotrops of carbon are amorphous carbon, crystalline graphite, and diamond. Franklin proposed a 2-dimensional structural concept on graphitic and non-graphitic carbons which are two typical examples of the sp² carbon group, as shown in figure I.19. [66–68] Such structural concept explains variable properties of two typical hard and soft carbons and their graphitizability which defines the graphitic extent, after their graphitization above 2500 ºC. The former carbon tends to stay as poor graphite while the latter one forms excellent graphite. The alignment of cluster units is particularly emphasized to be critical on the carbon graphitizability. [68]

**Amorphous carbon** or free, reactive carbon is an allotrop of carbon that does not have any crystalline structure. As with all glassy materials, some short-range order can be observed. **Glassy carbon**, also called **vitreous carbon**, can be fabricated in different shapes, sizes and sections, is a non-graphitizing carbon which combines glassy and ceramic properties with those of graphite.

![Figure I.19: Franklin models for (a) non-graphitizing (isotropic), (b) partially graphitizing and (c) graphitizing carbons](image)

Carbon foams are rigid, porous materials consisting of an interconnected network of ligaments. They can have open cell structure where pores are interconnected to one another or closed cell structure where pores are isolated from one another.
Partially graphitic carbon foams (figure I.20) were prepared from coal-based carbon precursor. [69] The carbon foam with graphitic structure (figure I.21) was synthesized by pitch based carbon (natural or synthesized pitch). [69]

![Figure I.20: SEM images of carbon foam derived from raw coal (a), coal solvent-extracts](image)

![Figure I.21: SEM images of carbon foam derived from (c), petroleum pitch (d), QI-free coal tar pitch](image)

Precursor used to synthesize carbon foams with amorphous structure is mainly thermosetting resins like polyurethane, phenolic, furfuryl, polyimides, etc. [46] Non-graphitizable or glassy carbon foams are shown in figure I.22

![Figure I.22: Glassy carbon foam (e) and (f) phenolic based carbon foam](image)

### I.6.3 Properties of carbon foams

Properties of graphitic and non-graphitic carbon foam are listed in table I.2. The most important properties are high temperature resistance, hardness (7 Mohs), low density, low electrical resistance, low friction, low thermal resistance, extreme resistance to chemical
attack and impermeability to gases and liquids. Glassy carbon is widely used as an electrode material in electrochemistry, as well as for high temperature crucibles and as a component of some prosthetic devices.

Table I.2: Properties of graphitic and non-graphitic carbon foam

<table>
<thead>
<tr>
<th>Properties</th>
<th>Graphitic carbon foams</th>
<th>Non-graphitic carbon foams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing cost</td>
<td>High due to requirement of high temperature, pressure and stabilization steps</td>
<td>Low and does not required special treatments</td>
</tr>
<tr>
<td>Nature</td>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Porosity</td>
<td>Up to 97 %</td>
<td>Up to 97 %</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.°k) [70]</td>
<td>0.05-210</td>
<td>0.085</td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>Above 20 (above 0.18 g/cc) [70]</td>
<td>1.42 (0.067 g/cc) [72]</td>
</tr>
<tr>
<td>Application temperature (°C),</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Air</td>
<td>3000 [73]</td>
<td>2500 [74]</td>
</tr>
<tr>
<td>Inert</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Co-efficient of thermal expansion (ppm/°C)</td>
<td>2-4 [71]</td>
<td>1.5 [70]</td>
</tr>
<tr>
<td>Permeability</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Machinability</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Major Applications</td>
<td>Heat exchangers for engine radiators, heat sinks and phase change materials, etc.</td>
<td>Porous electrodes, filters for metal, gas and various liquid filtration, etc.</td>
</tr>
</tbody>
</table>

I.6.4 Applications of carbon foams

Carbon and graphite foams are still relatively new, and have only been commercially available for approximately seven or eight years. As material becomes more available to industry, the list of potential applications will continue to grow; however, there are some
promising potential applications currently under development. [75] e.g. for fuel sinks, for fat
heat transfer, as battery electrode, radar adsorbing materials, thermal protection system,
nuclear shielding, etc.

**Rough Machining**

CFOAM [76] carbon foam block was glued and machined into the proper shape after
the adhesive was dried (figure I.23). However, this machined product should be undersized
from the actual dimensions to allow room for the composite surfacing material. The specific
under-cut will vary depending upon the type of surface being applied. Several different
surfacing materials have been developed and tested by Touchstone Company.

![Machinability of carbon foam block](image)

**Figure I.23: Machinability of carbon foam block**

**For Heat sinks**

Using carbon foam as core material for heat exchangers is shown in figure I.24; the
effective transfer of heat can be significantly increased while reducing size and weight of heat
exchanger. The large size and up-front location of radiators greatly increases the aerodynamic
drag of most vehicles. This can account for nearly 25 % of the fuel use in a heavy vehicle at
60 mph. The need for EGR (exhaust gas recirculation) cooling is expected to increase
radiator size by up to 30-40 % in some cases. Thus, development of smaller, lighter, and
more efficient radiators and EGR coolers will impact the styling, driver visibility, and the fuel
economy of a wide variety of trucks. [77]
Figure I.24: Carbon foam modular radiator with heat dissipation capacity of 33 kW

Figure I.25: Personal Cooling Devices made up of carbon foam (left), Schematic of evaporatively cooled computer chip (right)

Carbon foams also find application in personal cooling devices and fast heat transfer to cool computer chips as shown in figure I.25.

The Power Technology invented battery comprised of electrical current collectors constructed of reticulated vitreous carbon covered with a thin layer of a lead tin alloy. The current collectors create up to four times higher surface area for electrochemical reactions to take place compared to those in a typical lead acid battery, which results in a battery with
higher efficiency and higher capacity meaning more electricity is generated. A comparison of their current collector and a typical lead-acid battery collector grid is shown in the figure I.26. [78]

![Comparison of current collector and a typical lead-acid battery collector grid](image)

**Figure I.26:** Comparison of current collector and a typical lead-acid battery collector grid

The Oasis battery utilizes lightweight carbon foam plates instead of lead plates. These batteries offer longer service life, increased energy efficiency, and better performance under extreme conditions than traditional lead-acid batteries.

Carbon and graphite foams encompass a brand new material system with potential in a wide variety of applications including aerospace, offshore, military, power production and other commercial industries. Carbon foam is a sponge like carbon material with certain extraordinary features, such as light weight, high temperature tolerance (up to 3000 °C in inert atmosphere), high compressive strength, high permeability, large external surface area with uniform open cell structure, and adjustable thermal and electrical conductivity. The unique properties make carbon foam ultra-high performance engineering materials, and determine their many potential applications in numerous industries [75,79]: shipbuilding – living space modules, above deck structures, bulkheads; aerospace – aerospace modules, thermal protection systems, composite tooling, sandwich panels, radar adsorbing and antennae system; energy – fuel cells, battery electrodes, nuclear shielding, rods for nuclear reactors; automobile – catalytic converters; defence related – insensitive munitions, shields and body lightweight armour; medical – bone surgery material, prosthetics, tooth implants; architecture – insulation, fire proof blocks, shields and coatings, safe rooms, abrasives – for polishing of
glass and metal for paint removal, filters for hazardous conditions; electronics – processor radiators, radio frequency shields. [79,80]

There are number of way to fabricate carbon foam such as by carbonization of polymeric foams [81,82], from biomaterials like cork [83], olive stones [84], melamine [85], by using coal tar pitch [69,86], petroleum pitch [69], synthetic pitch from organics [87-89], coals [69,90], – provides an economical path for production of lightweight carbon materials. Combustion resistance is another key attraction of this material for researchers in both military and commercial applications. For example, carbon and graphite foams do not ignite, and their fire resistance is critical for offshore and naval applications where fires are a special concern.[91] The U.S. Navy is currently investigating its use in air intake and ventilation ducts, as ‘elevator’ floor for aircraft carriers and as lightweight ship hulls and other structures. [92] NASA is also evaluating carbon foam by conducting tests aboard the International Space Station to evaluate its use in future space applications. [93]

I.7 Functionalization of carbon foam

The surface of porous materials often needs to be modified for certain applications. It can be produced by physical or chemical method.

The chemical functionalization of carbon materials always was a challenge in chemistry and engineering. The term “functionalizing” generally refers to the introduction of functional groups to the carbon materials by acid treatment, controlled oxidation in air or steam or reactive gas, ozone treatment, plasma treatment, laser treatment, etc. Typical functional groups introduced in the course of method of preparation include, but are not limited to, the acidic groups like \(-\text{COOH}, -\text{CHO}, -\text{CO}, -\text{OSO}_3\text{H}, -\text{SO}, -\text{O}, -\text{OH}\) and also basic groups like quinone, pyrone etc. For the past few years, intensive research has been carried out both experimentally and theoretically for the identification of surface functional groups of the modified carbon materials [94-96], since these groups significantly facilitate
self-organization (aggregation in dyestuffs, laser toners), chemical stability (oxidative attack in structural applications), the reactivity towards stoichiometric (adsorbent) and catalytic processes (synthesis of small molecules, gas mask filters). The surface chemistry of activated carbon is basically determined by the amount and type of oxygen functionalities on surface. The oxygen functionalities can be introduced by treating the carbon with different oxidizing agents such as HNO\(_3\), (NH\(_4\))\(_2\)S\(_2\)O\(_8\), and H\(_2\)O\(_2\) [97-99]. Even though many spectroscopic techniques have been used to characterize the oxygen functionalities on carbon surface, information on these materials on molecular level is difficult to obtain. IR spectroscopy has been widely used to characterize these materials, even though there are technical difficulties in recording the spectra and in interpreting the spectra obtained. In order to overcome the difficulty in the interpretation of spectra, nowadays theoretically predicted assignments are employed.

I.8 Silica foam

I.8.1 Introduction

Porous structures in nature such as stems of plants, bones of animals, etc. are common and play important roles in mass transfer. [100] Materials organized with such macroporous structures can also minimize the channel blocking for fast diffusion of bulky molecules in industrial catalysis, adsorption, separation and waste disposing processes, etc., because they can effectively access the mesopores and/or micropores interconnected by macropores, especially in sticky systems. [100-107] Mesopores can provide selective or active sites for reactants, whereas existence of macropores can offer a highway for reactants accessing the sites with small pressure drops and benefit for obtaining intermediate product. For example, macroporous/mesoporous silica monoliths have been used in chromatographic separation systems. [108] For actually useful materials, the fabrications of porous materials with
required morphology, as well as having control of pore structures and compositions are much important.

Zeolites and related microporous (pore size < 2 nm) molecular sieves are widely used in industry as catalysts, adsorbents, ion exchangers, etc. Since they are produced in the form of very fine powders (μm), they give rise to excessive pressure drops over the reactors when charged as such. As a means to avoid this, fine zeolite particles are usually agglomerated into larger (mm) extrudates or granules using inert inorganic binders such as clay minerals, silica, and alumina. However, use of binders not only leads to dilution of the active zeolite species but also to pore blocking, diffusion limitation, and inaccessibility of active species within the interior of the agglomerated bodies. [109]

An alternative methodology to avoid pressure drops is to deposit zeolite films on the surfaces of supports with tailored macropores (pore size > 50 nm). [110-113] Although, zeolite film-coated macroporous supports usually have high mechanical strengths, the composites suffer from the low zeolite-to-support weight ratio, single-sided mass transport to and from the films, and easy loss of zeolite films from the supports upon repeated temperature swings, owing to the difference in their thermal expansion coefficients. As a means to overcome such practical problems associated with the applications of zeolites, there have been attempts to develop direct synthetic methods of preparing rigid, self-supporting zeolite monoliths with ramified macropores for easier internal molecular diffusion, [114-117] which can be classified as micro–macroporous mixed porous materials. [118-119] In conjunction with the above, recently a novel route to prepare large (>30 cm) monoliths of silicate, ZSM-5, and TS-1 foams having highly ramified networks of interconnecting macropores by applying polyurethane foams as templates. [120]

The room-temperature synthesis of a macro–mesoporous silica material during the natural creaming process of an oil-in-water emulsion is reported by T. Sen et al. [121] The
material has 3-dimensional interconnected macropores with a strut-like structure similar to meso-cellular silica foams with mesoporous walls of worm-hole structure. The material has very high surface area (~ 800 m$^2$/g) with narrow mesopore size distribution.

Wayne W. Lukens et al. [122] synthesized porous silica foams from polystyrene microspheres coated with cationic surfactants. The nature of foams depends strongly upon the synthesis conditions. Under basic catalysis, “closed-cell” foams were obtained. Under acidic catalysis, open-cell foams are obtained. The windows that connect cells of open-cell foams were believed to arise from direct contact between adjacent spherical templates.

Macro-porous silica foam was successfully produced by the sphere templating method. The scheme was based on assembling polystyrene particles into three-dimensional colloidal crystal, which was undergo suitable annealing treatment and functionalized with HTAB and used as template for silica sol-gel solidification. Porous silica foam was then obtained after removal of polystyrene template by calcination. The geometrical surface area of silica foam layer amounts 4 m$^2$/g which can be easily increased by using smaller polystyrene particles. [123]

Mesoporous silica foams having a macroporous skeleton and well-ordered internal mesoporous structure were synthesized by a novel vacuum-induced sol–gel process. This contrasts with the usual route involving expensive sacrificial microspheres. The resulting materials had a tri-modal pore size distribution and were characterized by nitrogen physic-sorption, X-ray diffraction, transmission electron microscopy. [124]

Tomita et al. [125] developed simple method for obtaining silica foam by combining sol-gel reaction and mechanical foaming without added organic pore formers in order to reduce generation of CO$_2$ and harmful gases by decomposition of organic compounds. Silica foam was prepared by mechanically foaming silica sol and controlling viscosity change and gelling. The gelation time of silica sol was varied from 10 minutes to 3 hours by changing
pH, temperature and concentration of surfactant added as a foam stabilizer. The dried silica gel foam was calcined at 600 °C and fired at 1000 °C to obtain sintered silica foam. The porosity and average pore size of silica foam was 84 % and 140 μm, respectively. The bending strength and gas permeability of the sintered silica foam was 2.4 MPa and $9.4 \times 10^{-11}$ m$^2$, respectively.

A process [126] for making foamed glasses and ceramics from sol-gels has been patented in US patent 0163472 A1. The method includes preparing a mixture of reactants capable of foaming a sol-gel with addition of a catalyst to control condensation stage followed by foaming using vigorous agitation in presence of surfactant. The gel body was dried at 130 °C and thermally stabilized at 600-800 °C to obtain consolidated macroporous material. Resulting structure comprises 3D network of spherical open pores that were thoroughly interconnected. SEM analysis showed macropore size in range of 10 -500 μm. It has potential for use as matrix in tissue engineering, in bone repair, and in organ regeneration BET surface area obtained was 150 to 454 m$^2$/g.

A low density silicate foam structure having a density of in the range 0.05 to 0.24 g/cc was reported in US patent 3844804. [127] The aqueous alkali metal silicate preferably comprises a combination of sodium silicate and potassium silicate, with potassium silicate comprising from about 5 % to 10 % by weight based on total weight of alkali silicate employed. Compressive strength varied in the range of 0.06 -0.08 MPa.

In present work, silica foam was synthesized by template route. Silica sol was used as silica precursor and PU foam was used as template.

I.8.2 Types and structure of Silica:

The chemical compound silicon dioxide, also known as silica (from the Latin silex), is an oxide of silicon with the chemical formula SiO$_2$. It has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell
walls of diatoms. [128,129] It has several polymorphs. Figure I.27 shows temperature and pressure conditions at which SiO₂ polymorphs are stable in a so-called phase diagram of SiO₂.

**Figure I.27: SiO₂ phase diagram[130]**

In majority of silicates, Si atom shows tetrahedral coordination, with 4 oxygen atoms surrounding a central Si atom. The most common example is seen in the quartz crystalline form of silica SiO₂. In each of the most thermodynamically stable crystalline forms of silica, on average, all 4 of the vertices (or oxygen atoms) of the SiO₄ tetrahedra are shared with others, yielding the net chemical formula: SiO₂.

SiO₂ has a number of distinct crystalline forms (polymorphs) in addition to amorphous forms as shown in figure I.28. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO₄ units linked together by shared vertices in different arrangements.
Figure I.28: Different crystal structure of silica (red – oxygen atoms, Grey – silicon atoms)

Silicon-oxygen bond lengths vary between different crystal forms, for example in α-quartz, bond length is 161 pm, whereas in α-tridymite it is in the range 154–171 pm. The Si-O-Si angle also varies between a low value of 140° in α-tridymite, up to 180° in β-tridymite. In α-quartz the Si-O-Si angle is 144°. [131]

Theoretical, at normal pressure trigonal quartz (α-quartz) transforms into hexagonal β-quartz at 573°C, upon further heating SiO₂ will transform into hexagonal β-tridymite at 870°C and later to cubic β-cristobalite at 1470°C. At 1705°C β-cristobalite finally melts: (figure I.29)
Silica is manufactured in several forms including fused quartz, crystal, fumed silica (or pyrogenic silica, trademarked Aerosil or Cab-O-Sil), colloidal silica, silica gel, and aerogel. Silica is used primarily in the production of glass for windows, drinking glasses, beverage bottles, and many other uses. The majority of optical fibres for telecommunications are also made from silica. It is a primary raw material for many whiteware ceramics such as earthenware, stoneware, porcelain, as well as industrial Portland cement. Silica is a common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. It is the primary component of diatomaceous earth which has many uses ranging from filtration to insect control.

1.8.3 Sol-gel processes:

Silica sol was used for the preparation of silica foam. Sol-gel processes can be used to prepare variety of materials, including: powders, films, fibers, and monoliths. Traditionally, sol-gel process involves hydrolysis and condensation of metal alkoxides. Metal alkoxides have the general formula M(OR)x and an alkoxides ion is the conjugate base of an alcohol.

1.8.3.1 Polymerization of Metal Alkoxides:

Metal alkoxides are members of organometallic compounds family, which are organic compounds and have metal atoms in the molecule. Metal alkoxides (ROM) are like alcohols (ROH) with a metal atom M replacing the hydrogen H in the hydroxyl group. They constitute the class of chemical precursors most widely used in sol-gel synthesis. Metal alkoxide are ideal chemical precursors for sol-gel synthesis because they react readily with water. The
reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom as follows:

The most thoroughly studied metal alkoxide is silicon tetraethoxide, or tetraethyl orthosilicate (TEOS) as a precursor of silica. The chemical formula for TEOS is given by: \( \text{Si(OC}_2\text{H}_5)_4 \), or \( \text{Si(OR)}_4 \) where the alkyl group \( R = \text{C}_2\text{H}_5 \).

\[
\text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OR)}_3 + \text{R-OH}
\]

Depending on the amount of water and catalyst present, hydrolysis may proceed to completion, so that all OR groups are replaced by OH groups, as follows:

\[
\text{Si(OR)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{ROH}
\]

Any intermediate species \([\text{OR)}_2 - \text{Si} - (\text{OH)}_2\) or \([\text{OR)}_3 - \text{Si} - (\text{OH})\] would be considered the result of partial hydrolysis. Two partially hydrolyzed molecules can link together in a condensation reaction to form a siloxane \([\text{Si} - 0 - \text{Si}]\) bond:

\[
\text{(OR)}_3 - \text{Si} - \text{OH} + \text{HO} - \text{Si} - (\text{OR)}_3 \rightarrow [(\text{OR)}_3\text{Si} - (\text{O} - \text{Si (OR)}_3] + \text{HOH}
\]

or

\[
\text{(OR)}_3 - \text{Si} - \text{OR} + \text{HO} - \text{Si} - (\text{OR)}_3 \rightarrow [(\text{OR)}_3\text{Si} - (\text{O} - \text{Si (OR)}_3] + \text{ROH}
\]

Thus, polymerization results from the formation of a 1, 2, or 3- dimensional network of siloxane \([\text{Si} - O - \text{Si}]\) bonds accompanied by the production of HOH and ROH species.

By definition, condensation liberates small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon-containing molecules by the process of polymerization. Thus, a polymer is a huge molecule (or macromolecule) formed from hundreds or thousands of units called monomers. Polymerization of silicon alkoxide, for instance, can lead to complex branching of the polymer because a fully hydrolyzed monomer \( \text{Si(OH)}_4 \) is tetrafunctional (can branch or bond in 4 different directions). Alternatively, under certain conditions (e.g. low water concentration) fewer than 4 of the OR or OH groups (ligands) will be capable of condensation, so relatively little branching will occur. The
mechanisms of hydrolysis and condensation, and the factors that bias the structure toward linear or branched structures are the most critical issues of sol-gel science and technology. [139]

1.8.3.2 Advantages of the sol-gel process [140]

- It provides high purity homogeneous materials
- It offers an easy way for the introduction of trace elements
- It allows the use of chemical techniques for reaction control
- It allows formation of a “pre”-inorganic network in solution
- It allows densification to inorganic solids at comparatively low temperatures

1.8.3.3 Disadvantages of the sol-gel process [140]

- High cost of the precursors;
- Long process duration;
- Difficulties in the synthesis of monoliths;
- Difficulties in the process chemistry with respect to properties control and reproducibility.

1.8.4 Applications of silica foam:

The material has high chemical purity, good acid resistance, excellent electrical resistance and is unaffected by nuclear radiation. Because it’s such a good heat barrier, fuel economy will result from the use of silica foam as compared to conventional refractories and castables. Typical applications include furnace door, roof, and wall insulation, aluminium trough liners, reflectors for quartz lamps and infrared heaters, high temperature gas filters, molten metal filtration, tooling for aerospace and glass forming operations, brazing fixtures, gas uptake liners, and thermal barriers for nuclear applications. Silica foam can withstand moderate working face conditions including trough linings for molten aluminium, copper, and other non-ferrous alloys.
1.9 Scope of present work:

In present work, carbon foams were prepared using polymeric template method. Commercially available open cell PU (polyurethane) foams were used as template and these were impregnated with phenolic resin. The cured foams were carbonized in inert atmosphere and characterized. It was seen that both ether and ester type polymeric foam produce carbon foam with good mechanical strength. Also, silica foams were prepared using template method. Porous silica foam was synthesized by impregnation of silica sol in to commercial available polymeric foams template having well-ordered structure. By controlling processing conditions, porous silica monoliths with interconnecting porosity with various macroporous structures can be obtained. In this case ether type polymeric foam gives silica foam with good mechanical properties. Thus, the selection of appropriate template and processing parameters would enable fabrication of carbon and silica foam with desired range of porosity, pore size distribution and pore morphology and properties required for specific application.

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Chapter I