CHAPTER 1

Polymer Based Syntactic Foams-An Overview

This chapter compiles literature survey on polymer based syntactic foams. The basics of syntactic foams, general methods of preparation and properties of syntactic foams, types of syntactic foams, recent advances in this field and applications of syntactic foams are covered. Different polymer systems have been discussed. The scope and objective of the thesis are also presented.
1.1 Composites

Materials with a specific set of properties are required to meet the demands of modern applications. It is not possible for a particular type of material to exhibit all the desired properties. This led to the development of “composite materials”, which are formed by a combination of two or more materials to get properties superior to those of the constituents. By definition, “composite materials constitute a mixture of two or more materials which possess significantly different properties as compared to each other”. Composite materials are characterised by their high strength-to-weight ratio, high bending stiffness, corrosion resistance, excellent fatigue characteristics and good thermal insulation properties. The properties of composites can be tailored according to specific design requirements, directional and spatial properties [Agarwal and Broutman, 1990; Chung, 2004; Gay et al., 2003; Kaw, 1997; Matthews and Rawlings, 1999].

The applications of composite materials are numerous. They have gained popularity in high-performance products that need to be lightweight, yet strong enough to endure harsh loading conditions such as in aerospace components. Other uses include insulation materials, fishing rods, storage tanks, baseball bats, bicycle frames and bodies etc. Carbon composite is a key material in today's launch vehicles and spacecrafts. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles [Devi, 2007; Salkind and Holister, 1973; Zagaïnov and Lozino-Lozinskiï, 1996].

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials in composites viz. the matrix phase and the reinforcing phase (which is in the form of fibres, sheets, or particles). The matrix material surrounds and supports the reinforcement materials by
maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination depending upon the requirement [Matthews and Rawlings, 1999; Strong, 1989].

1.2 Matrices used in composites

The matrix material used in composites can be polymer, ceramic or metal. A basic requirement for matrix material is that its strain at break must be larger than that of the fibres it is holding. The most common material with these characteristics is polymers. Therefore, over 90% of the modern composites have polymeric materials as their matrix. Ceramic and metal matrices are most often used when polymer matrices will not suffice, usually because of their temperature limitations [Strong, 1989]. This thesis focuses mainly on polymer matrix based composites.

Polymer matrices are generally classified into thermoplastics and thermosets. Thermoplastics are plastic materials that soften upon heating and harden upon cooling. The process is reversible and the material can be remoulded by heating. Thermoplastics have no chemical bond between their long chain molecules. The polymer chains in thermoplastics are held together by weak van der Waals forces. Examples of the thermoplastic resin matrices used include polyethylene, polypropylene, polystyrene, nylons etc. Thermosetting polymers are plastic materials that “set” or cross link upon heating. The cross linking process actually is the formation of chemical bonds between the long carbon chains. The cross-linking process is irreversible. Once set, the thermosetting plastic cannot revert to its prior stage. Thermosets are currently the
predominant matrix resin for composites due to their availability, well established processing technologies, existence of large database and low material cost. The important thermosetting polymers are epoxies, phenolics, bismaleimides, cyanate esters etc. [Chung, 2004; Mucccio, 1999].

1.2.1 Epoxy resin

Epoxy resins are characterised by the presence of at least two epoxy (or oxirane) groups within their molecular structure. They are typically formed by the reaction of compounds containing at least two active hydrogen atoms (polyphenolic compounds, diamines, amino phenols, heterocyclic imides and amides, aliphatic diols etc) and epichlorohydrin [Odian, 2004]. The synthesis of diglycidyl ether of bisphenol A (DGEBA), the most widely used epoxy resin is illustrated in Scheme 1.1. A variety of coreactants are used to cure epoxy resins, either through the epoxide or hydroxyl groups. The widely used curing agents are polyamines, polyamides, polysulfides, urea- and phenol-formaldehyde, acids or acid anhydrides etc. [Billmeyer, 2003]. The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties.

Scheme 1.1 Typical synthesis of an epoxy resin
In general, epoxies are known for their excellent adhesion, chemical and moderate heat resistance, excellent mechanical properties and good electrical insulating properties. The applications of epoxy based materials are extensive and include coatings, adhesives and composite materials such as those using carbon and glass fibre reinforcements. Epoxy adhesives are a major part of the class of adhesives called "structural adhesives". These high performance adhesives are used in the construction of aircrafts, automobiles, bicycles, golf clubs, skis, snowboards, and other applications where high strength bonds are required. In the aerospace industry, epoxy resin is used as a structural matrix material which is then reinforced by fibre. Typical fibre reinforcements include glass, carbon, kevlar, and boron. Light weight rocket motor cases use combinations of kevlar and epoxy system. Satellite support structures, antenna, yoke and solar panel substrates are preferably made of epoxy composites. Epoxy resin is also used in manufacturing the rotor blades of wind turbines [Devi, 2007; Odian, 2004].

1.2.2 Phenolic resins

As the first commercial synthetic resin, phenolic resins have been extensively studied for several years and are still the best commercially available resin. Phenolic resins have several desirable characteristics, such as superior mechanical strength, heat resistance and dimensional stability, as well as, high resistance against various solvents, acids and water. They evolve low smoke upon incineration and are known for high char yielding properties. The most common types of phenolic-based prepolymers are resoles and novolacs. Syntheses of resole and novolac prepolymers are carried out using phenol or its derivatives and formaldehyde under basic or acidic conditions. Novolacs are formed under highly acidic conditions with an excess of phenol. Resoles are synthesised
under basic conditions with an excess of formaldehyde. The conversion of novolacs into insoluble and infusible networks requires catalysts, whereas resoles require only heating over a certain period. The phenolic networks are highly aromatic and are thus resistant to thermal oxidation [Hale et al., 1989; Knop and Scheib, 1979; Nair et al., 1997; aNair et al., 2001; Nair, 2002; Nair, 2004; Sandler and Karo, 1992; aWang et al., 2005].

Phenolic resins have been playing an important role as matrix in composite materials for thermo-structural and ablative applications. These excellent properties originate from the chemical structure, which is primarily made up of C-C bonds that are present in aromatic rings, which are characteristics of phenolic groups. Under thermal stress, phenolic structure slowly breaks up releasing carbon. Fibre reinforced phenolic resin composites are used in thermal protection systems such as spacecraft heat shields for atmospheric re-entry, rocket motor nozzle lines, missile magazines, and blast deflectors due to their excellent ablation resistance and mechanical properties. Phenolic resins have entered into other technological areas as composites for automobile, transportation, electrical and electronics applications. Phenolic resins compete very well with urea-formaldehyde bonded plywood and most of the plywood made today is phenolic resin based. Phenolic resins are used as paint and varnish, coatings, composite wood materials, industrial laminates, paper impregnation, foundry resins, abrasive materials and in rubbers and adhesives [Gardziella et al., 2000; Goodman, 1998; Fukada, 1996; Kopf and Little, 1988; bWang et al., 2005].

Conventional phenolic materials from either novolac or resole type resins suffer from the common shortcomings of brittleness and release of volatiles upon curing via condensation reactions [aWang et al., 2005; bWang et al., 2005]. This necessitates the application of pressure during compression moulding and makes them unsuitable for resin transfer mould (RTM) process [Nair et al., 2002]. In addition, the cured materials
have low thermo-oxidative stability. To solve these problems and to meet the ever-increased performance and novel processes (such as RTM requirements), novolac resins have been functionalised with proper active groups, to make them crosslinkable via addition mechanism instead of condensation. One such polymer is propargyl ether novolac (PN) whose synthesis and curing are shown in Scheme 1.2. PN resin is synthesised by the reaction between novolac and propargyl bromide in presence of $K_2CO_3$ and a phase transfer catalyst in acetone. The resin cures by an addition reaction of the propargyl group by a complex mechanism. The cured resin is stable up to 400°C, unlike the condensate-cured one which starts losing weight at about 300°C [Bindu et al., 2001]. PN resins are attractive from the standpoint of easy synthesis, addition cure and high thermal properties. In the last decade, PN resins and their blends have been explored as candidate matrices for advanced composites in thermo-structural and thermal shielding applications [Dougus and Overend, 1994; Grenier-Loustalot and Sanger, 1997; Wang et al., 2005]. Similar addition curable phenolic resins functionalised with respect to groups such as allyl group [Wang et al., 2006], phenyl maleimide [Nair et al., 2000], acetylene [Nair et al., 2002], phenyl ethynyl [Nair et al., 2001] etc. have been reported.

Polybenzoxazine is another class of addition cure phenolic system based on oxazine-modified phenolic resin that undergoes a ring-opening polymerisation. It is a novel class of thermosetting polymer having good physical and thermal properties. It overcomes many shortcomings associated with conventional phenolic resins. In general, they possess excellent resistance to chemicals and UV light and have high $T_g$ when compared to conventional phenolic resins. Benzoxazines are generally synthesised from phenol, aniline and formaldehyde, by Mannich reaction. The synthesis and curing of bisphenol A based benzoxazine is shown in Scheme 1.3. Here, the polymerisation
occurs by the ring opening polymerisation of benzoxazine ring [Ishida and Allen, 1996; Ishida and Rodriguez, 1995; Kim and Ishida, 2001; Kumar, 2008; Macko and Ishida, 2000].

Scheme 1.2 Synthesis and curing of PN resin

Scheme 1.3 Synthesis and curing of benzoxazine monomer
1.2.3 Bismaleimides

Bismaleimides are addition-type polyimides used in high performance structural composites requiring higher temperature use and increased toughness. Monomers are usually synthesised from maleic anhydride and an aromatic diamine and the bismaleamic acid formed is cyclodehydrated to a bismaleimide resin (Scheme 1.4). The double bond of the maleimide is very reactive and can undergo chain extension reactions. Bismaleimides can provide a higher service temperature than epoxies, while maintaining epoxy like processing [Lin and Chen, 1996].

Bismaleimides have glass transition temperatures in excess of 260°C and continuous-use temperature of 200-230°C. They find applications in high-performance structural composites and adhesives for aircraft, aerospace and defence applications where temperatures beyond 150-180°C are experienced [Odian, 2004].

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\text{Scheme 1.4 Synthesis of a bismaleimide monomer}
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1.2.4 Cyanate Esters

Cyanate esters have received considerable attention owing to their desirable chemical, electrical and mechanical properties. Their high glass transition temperature (250-300°C), fracture toughness, thermo-oxidative stability and retention of mechanical properties at high temperature make them attractive in aerospace applications. The low out gassing, minimal dimensional changes during thermal cycling, good long term
stability, self adherent properties to honeycomb and foam cover, and high service
temperature are the key advantages of cyanate resin over the state-of-the-art epoxy resin
[Nair et al., 2001; dNair et al., 2001].

Cyanate esters are synthesised by the reaction of phenolic compounds with
cyanogen halides. Cyanate esters cure by a thermal/catalytic cyclotrimerisation reaction
to form a triazine network known as polycyanurate (Scheme 1.5). They are known to be
catalysed by a numbers of materials including transition metal carboxylates, acetyl
acetonates, phenols, metal carbonyls, etc. Generally, they are cured with a transition
metal catalyst or chelate catalyst in presence of a hydrogen donor such as nonyl phenol
[Nair et al, 2001].

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\text{NCO-Ar-OCN} \rightarrow \quad \text{Polycyanurate Network}
\]

**Scheme 1.5 Polymerisation reaction of cyanate ester monomer**

Cyanate ester finds application in electronics, printed circuit boards, satellites
and aerospace structural composites. They have been successfully employed in
composite structures in INTELSAT [Devi, 2007]. Several major space and radome
manufacturers have qualified cyanate ester resins despite the extensive database on epoxies and the inherently conservative nature of the industry [Hamerton and Hay, 1998].

1.3 Types of composites

The properties of composites depend primarily on the amount, arrangement and type of reinforcement in the matrix. Depending on the constituent materials, composites can be broadly classified into fibre reinforced composites, sandwich composites and particulate reinforced composites [Katz and Milewski, 1987].

1.3.1 Fibre reinforced composites

Fibre reinforced composites consist of fibres of high strength and modulus embedded in or bonded to a matrix with distinct interfaces between them. The fibres are the principal load bearing component while the matrix keeps them in the desired location and orientation. Both fibres and matrix retain their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents alone. The fibres can be made of polymer, ceramic, glass etc. Sometimes, fillers or modifiers might be added to smooth manufacturing process, impart special properties, and/or reduce product cost. The fibres can be incorporated into a matrix either in continuous lengths or in discontinuous (chopped) lengths [Biron, 2004; Katz and Milewski, 1987; Mallick, 1993; Mouritz and Gibson, 2006; Tong et al., 2002].

Fibres increase the modulus of the matrix material. The strong covalent bonds along the length of fibre give them a very high modulus in this direction as to breaking or extending the fibre, needs breakage of the bonds. The property varies depending on
the direction in which they are measured. In general, fibres have a very high modulus along their longitudinal axis, but have a very low modulus perpendicular (transverse) to their axis. Fibre reinforced composites are expensive to manufacture and are used in aerospace, sports equipments and race cars and generally not suitable for curved shaped components or structures.

The arrangement or orientation of the fibres relative to one another, the fibre concentration, and the distribution all have a significant influence on the properties of fibre-reinforced composites. Applications involving totally multidirectional applied stresses normally use discontinuous fibres, which are randomly oriented in the matrix material. Consideration of orientation and fibre length for a particular composite depends on the level and nature of the applied stress as well as fabrication cost.

1.3.2 Sandwich structured composites

A sandwich structured composite is a special class of composite material that is fabricated by attaching two thin but stiff skins to a lightweight core. The core material is normally a low strength material, but its higher thickness compared to the skin provides the sandwich composite with high bending stiffness with an overall low density. Open and closed cell structured foam, balsa wood and composite honeycomb are the commonly used core materials. Glass or carbon fibre reinforced laminates are widely used as skin materials. Sheet metal is also used as skin material in some cases. Special care needs to be taken when selecting the skin because it comes in direct contact with the working environment. Depending on the application, the skin and the core can be of the same material or of different materials. The mechanical properties of sandwich composite structure depend on the skin, the core and the bonding between them. These properties could vary significantly depending on the assembly and manufacturing
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1.3.3 Particulate reinforced composites

Particulate reinforced polymer composites consist of a continuous matrix phase reinforced with one or more types of particulate reinforcements [Maharsia, 2005]. Particles used for reinforcing include ceramics and glasses, small mineral particles, metal particles such as aluminium and amorphous materials including polymers and carbon black [Gupta, 2003; Katz and Milewski, 1987]. Appropriate choice of fillers can produce composites with superior strength, damage tolerance, wear resistance and chemical resistance. The particles in these composites help to increase the modulus of the matrix, decrease the ductility and permeability of the matrix. These composites are less expensive when compared to fibre reinforced composites. Examples of particulate composites include polymer matrix containing aluminium, steel or glass particles [Lee, 1993; Maharsia, 2005; Rothon, 2003].

Another most important class of particulate reinforced composites is syntactic foam which forms the basis of study of this thesis. A detailed description of syntactic foams can be found in the following sections.
1.4 Syntactic foam—Definition

Syntactic foams are composite materials in which hollow microspheres are embedded in a matrix. The term “syntactic foam” was introduced in 1960's. “Syntactic” is derived from the Greek word “syntaktikos”, meaning “to arrange together”. The term ‘foam’ is used simply because of the cellular nature of the material. Syntactic foams are also known as foam composites since the hollow microspheres can be viewed as reinforcements in a matrix [Gupta et al., 2001; Karthikeyan et al., 2001; Long and Mitchell; Luxmoore et al., 1976].

Incorporating hollow particles having a lower density compared to binder material, allows for the manufacture of light-weight materials with the increase of the filler content. Thus, syntactic foam with a filler density that is lower compared to the binder can be considered as a special type of particulate-filled polymer composite. Syntactic foams are categorised as physical foams because the matrix is not foamed chemically but the gas containing particles are filled mechanically into the matrix. They have the real advantage of being fabricated over a large density range and possess useful properties that can be tailored for specific applications [Ashida, 1995; Gupta et al., 1999; Karthikeyan et al., 2001; Wouterson et al., 2005].

1.4.1 Matrices used in syntactic foams

The matrices used in syntactic foams include polymers, metals or ceramics. In this thesis, the focus is mainly on polymeric matrix based syntactic foams. Both thermoplastic and thermosetting polymers have been employed to process syntactic foams. In fact, syntactic foams are mainly prepared by using thermosetting matrices because of the favourable processing conditions avoiding breakage by gently blending the hollow microspheres with the thermoset precursors of very low viscosity. From the
processing point of view, thermosetting syntactic foams have many advantages compared to thermoplastic ones. For example, thermosetting syntactic foams can be processed at much lower temperatures compared to thermoplastic syntactic foams, thereby reducing the material and energy costs for processing. Also, thermosetting resins have less solvent sensitivity and are not negatively affected by cleaning solutions [Harrison et al., 2000]. Nevertheless, some attempts have been made to process syntactic foams with a thermoplastic matrix by using a solvent, or even by using a twin-screw extruder [Fine et al., 2003].

1.4.2 Microspheres in syntactic foams

The hollow microspheres give the syntactic foam its low density, high specific strength, low moisture absorption etc. The microspheres may be made up of glass, polymer, carbon, ceramic, or even metal. Other terminologies are also used in literature to describe microspheres; like microballoons and cenospheres. The microspheres have a burst pressure sufficient to withstand the forces imposed upon them during the formulation, mixing and dispensing processes. The main processing advantage of microspheres is that the viscosity of the systems with spherical fillers is always less than that of systems with fillers of any other shape. The properties like high temperature resistance, good strength-to-weight ratio, clean surface chemistry, narrow particle distribution, low thermal conductivity, low dielectric constant, low dissipation factor etc. make microballoons an important reinforcing material or additive in these composites [Kishore et al., 2005; Shutov, 1991].

Microspheres are characterised by their particle size, wall thickness and density. The microballoon wall thickness is related to a parameter named ‘radius ratio’, η which
is defined as the ratio of the inner radius, $r_i$, to the outer radius, $r_o$, of the microballoons, as defined in the equation,

$$\eta = \frac{r_i}{r_o}$$

where $r_i$ is the inner and $r_o$ is the outer radius of the microballoon respectively. Increase in radius ratio corresponds to a decrease in wall thickness, which leads to a decrease in true particle density of microballoon. Therefore, microballoons having higher radius ratio give rise to lower density syntactic foams and vice versa [Woldesenbet et al., 2005].

The most commonly used microspheres in syntactic foam are glass microspheres due to their high specific strength, regularity of the surface, good wetting characteristics and low viscosity of the resin-microballoon mixture, energy absorption properties, low cost and ease of fabrication [Katz and Milewski, 1987; Matthews, 1994; Rizzi et al., 2000]. Also, hollow glass particles have very low densities as compared to corresponding hollow metallic and ceramic particles [Ashida, 1995]. In general, syntactic foams based on glass microspheres exhibit better mechanical properties than those made with polymeric microspheres due to the substantial difference between elasticities of glass and polymer.

Polymeric microballoons are commonly made up of epoxy resin, unsaturated polyester resin, silicone resin, phenolics, melamine-formaldehyde, polyvinyl chloride, polypropylene, polystyrene etc. [Kishore, 2005; Puterman et al., 1980]. As a general rule, these microspheres are produced by spraying low-viscosity solutions and melts [Shutov, 1991]. Among the various polymeric microballoons, phenolic microballoons have been widely used for processing syntactic foams. The main advantage of phenolic
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microspheres over those of glass is their lower density. Syntactic foam made of phenolic microballoons and polydimethyl siloxane (PDMS) is used in ISRO for thermal insulation of heat shield of launch vehicles and for cryogenic tanks. Another type of polymeric microballoons based on polyvinylidene chloride (PVDC) known as saran microspheres are mechanically tougher and have high resistance to organics. Ultra low-density resilient PVDC hollow microspheres can be premixed in polyester and stored for long periods. They also find application in urethane and epoxy foams [Melber et al., 1984].

Organic microspheres are also used in syntactic foams. They suffer from so many limitations and hence their use is quite limited. Some organic microspheres can be converted into carbon microspheres. Usually, these spheres are derived from phenolic microspheres or carbon pitch spheres. The conversion of the organic spheres to carbon microspheres is usually accomplished by heating in an inert atmosphere to a temperature of 800-1000°C. This is sufficient to convert the bulk of the organic material to carbon, but in order to get graphitisation, further heating to temperatures above 2000°C is performed. Carbon microspheres obtained from phenolic resins have densities around 150 kg/m³ while those obtained from pitch sources have densities of 50-250 kg/m³ [Puterman et al., 1980]. Materials made from carbon microspheres of low apparent density have a substantially lower thermal conductivity (0.049-0.064 W/m.K) for densities of 200-300 kg/m³) than other syntactic foams [Shutov, 1991].

Another type of microballoon known as shirasu microballoon is the yield of secondary popping expansion of volcanic ash sand particularly available in Kagoshima, Japan [Takeuchi, 2003]. Fly ash in the form of hollow particles is also used in syntactic foams [Puterman et al., 1980]. The Philadelphia Quartz Company (USA) produces “Q-
Cel” quartz microspheres which are mechanically very strong and are very cheap (half the price of glass and 1/3 the price of phenolic microspheres). Metal, metal oxide and metal salt microspheres have also been used in syntactic foams [Shutov, 1991].

### 1.4.3 Structure of syntactic foams

Syntactic foams are normally tertiary systems, since the matrix and the gas-filled microspheres are usually made of different materials. However, they are basically classified as two-phase systems and three-phase systems [Rizzi et al., 2000]. The close packed arrangement of hollow microspheres in the matrix gives rise to two-phase syntactic foams. The two-phase structure is schematically shown in Figure 1.2(a). However, this is only a hypothetical situation. During the processing of syntactic foams, there is possibility for entrapment of air, which leads to voids in the foam structure. The existence of voids makes syntactic foams, a three-phase system unlike conventional polymer foams, which are binary [Gupta et al., 1999; Calahorra et al., 1987]. The three-phase structure is schematically shown in Figure 1.2(b). Thus, two-phase syntactic foams consist of hollow microspheres dispersed in a resin, whereas three-phase syntactic foams consist of hollow microspheres dispersed in a resin containing finely dispersed air bubbles.

### 1.4.4 General methods for preparation of syntactic foams

The general methods for the preparation of conventional polymer foams require the use of at least two chemical constituents: one to decompose into a gas to form the bubbles, and one to form the walls of the cells. Syntactic foams use “prefabricated,” microballoons or microspheres that are mechanically combined with a resin to form a composite material i.e., syntactic foams can be processed by simply incorporating microballoons in a matrix. The common methods used to prepare syntactic foams differ
from those used for preparation of other polymer composites. The hollow glass, organic or carbon microspheres do not withstand high pressures. Therefore, it is practically impossible to extrude or injection mould mixtures containing hollow microspheres. A variety of manufacturing techniques are available for processing syntactic foams, which varies from simple blending of the components to novel coating methods of the resin on the microsphere surface [Puterman et al., 1980]. The microballoon concentration and resin-binder composition are found to be crucial to the ease of manufacturing syntactic foams [Bunn and Mottram, 1993]. The choice of process parameters (temperature, mixing time, and addition sequence) is also a main challenge in the processing of syntactic foams [Shutov, 1991].

Figure 1.2 Schematic representation of (a) two-phase and (b) three-phase structures of syntactic foam [Gupta et al., 1999]
The binder materials used in syntactic foams must have low viscosity, easily controlled gelation time, small exothermal effect during curing, low curing shrinkage, good adhesion and wettability to the filler and compatibility with modifiers and fillers, including diluents, plasticisers, dyes, and flame retardants [Shutov, 1991].

A common method for the preparation of syntactic foams is by impregnation of microspheres in a resin solution. This method ensures uniform coating of each sphere by resin and hence homogeneous dispersion of the resin among the microspheres is achieved. The main difficulty of this method lies in the need to entirely remove the solvent prior to the final curing. However, this method has many drawbacks, like potential environmental safety and health hazards of volatile solvents, formation of defects and structural non-uniformities when the solvent is being driven off by heat from the interior of the syntactic foam, difficulty in obtaining batch-to-batch reproducibility and additional energy or cost associated with transporting the solvent-laden pasty mass to the moulding or curing equipment [Matthews, 1994].

When the resin is available in a powdery form, a solid mixture of the hollow microspheres and the resin powder is prepared first. Then, a weighed quantity of the solid mixture is transferred to a mould of predetermined volume, pressed and cured [Puterman et al., 1980].

A coating method has also been used for processing syntactic foams which consists of resin coating, vacuum filtration and polymer precipitation. In the coating step, a thin film of the polymeric solution is adsorbed onto the sphere surface. Precipitation of the polymer at this stage would lead to undesired agglomeration. The slurry is then vacuum filtered and rinsed with liquids while on the filter. The purpose of this liquid rinsing step is to precipitate the polymer on the sphere surface and to
simultaneously remove the solvent by leaching. Vacuum drying of the coated spheres gives a moulding powder of discrete particles. By this method, uniform resin coating is achieved on the spheres which will subsequently lead to uniform resin distribution in moulded articles [Cravens, 1973].

The processing of syntactic foams from liquid thermosetting resins, without using solvent has also been reported. The use of liquid resin materials in polymeric foam materials has some disadvantages. For example, liquid resin materials when used to form syntactic foams do not produce highly uniform distributions of the solid materials in the foam. The mixture is heated to allow the thermosetting resin to flow and wet the microballoons in the mixture. The mixture is then cured to set and crosslink the thermosetting resin to form the syntactic foam. This method has been used for liquid polyesters and silicones [Harrison et al., 2000].

Easily removable, environmentally safe and low-density syntactic foams are prepared by mixing insoluble microballoons with a solution of water and/or alcohol-soluble polymer to produce pourable slurry. Vacuum filtering the slurry in varying degrees removes unwanted solvent and solute polymer. Finally, drying removes the residual solvent. The method is used when the solute polymers are non-toxic and soluble in environmentally safe solvents such as water or low-molecular weight alcohols. The syntactic foams produced by this method are particularly useful in those applications where ease of removability is beneficial, and could find application in packaging of recoverable electronic components, in drilling and mining applications, in art works, in the entertainment industry for special effects, in manufacturing as temporary fixtures etc. [Arnold et al., 1995].
Spraying methods on a surface of a liquid resin stream and a microballoon stream meeting at some point while still in the air, are also possible. This will produce discrete resin coated particles which behave as a free-flowing material, serving as a regular moulding powder [Mukherjee and Saraf, 1994].

Cornerstone Research Group (CRG), Inc has developed a unique process to produce strong yet lightweight syntactic foams. This process involves a low-stress resin removal system in which, the excess resin is extracted from the syntactic material before the resin is cured. Along with the excess resin, any microspheres that may have been broken during the mixing process are also removed. The resulting foam has low density and low void content, essential for high integrity composites [http://www.crgrp.com/syntactics.shtml]

1.4.5 Properties of syntactic foams

Syntactic foams possess many advantageous properties compared to conventional polymer foams and composites. The application of syntactic foams has centered around their ability to reduce weight, increase stiffness, exhibit buoyancy, provide good nailability and screwability and in reducing cost [Anderson et al., 1970; Gupta et al., 2005]. Syntactic foams are mechanically superior due to the rigidity of the microballoons. Hence, syntactic foams stand in between conventional reinforced polymeric materials and foams with very high specific strengths [Karthikeyan et al., 2004; Karthikeyan et al., 2007]. A number of other foamed materials offer better thermal insulative properties but none offer simultaneous high-strength properties [Ferguson and Shaver, 1970]. They have excellent compressive and hydrostatic strength, good impact behaviour and damage tolerance compared to other closed cell structured materials, which makes them very attractive for structural applications
[Gupta et al., 2002; Gupta et al., 2005; Marur, 2005]. They are found to be highly strain rate sensitive, in contrast to metallic foams [Woldesenbet et al., 2005].

1.4.5.1 Comparison with conventional foams

Blown and self-expanding foams develop a fairly random distribution of gas pockets of widely varying sizes and shapes. But the porosity of syntactic foams can be much more closely controlled by careful selection and mixing of the microballoons with the matrix. As the voids in syntactic foams are due to the cellular structure of the microsphere, it is easier to predetermine and control the size and size distribution of the voids within syntactic foam [Mukherjee and Saraf, 1994; Puterman et al., 1980]. While ordinary foams are visibly porous, syntactic foams have cells so small that the material looks like a homogeneous solid. In conventional foams, the cells are partially or fully connected whereas in syntactic foams, the voids are enclosed within the walls of the microspheres and are therefore isolated from each other. Porosity of syntactic foams is typically at the microscopic level [El-Hadek and Tippur, 2003].

1.4.5.2 Property tailoring

The properties of syntactic foams can be tailored by changing a wide variety of parameters, which include the matrix and microballoon materials, size and size distribution of microballoon, wall thickness and volume fraction [Bunn and Mottram, 1993; Gupta, 2003; Gupta et al., 2004; Gupta and Ricci, 2006]. The composition and density of syntactic foams can be predicted as these are fabricated by filling mechanically the gas containing particles into the polymer matrix. Unlike most other foams, syntactic foam is a material whose density before curing is the same as that after curing [Wouterson et al., 2005]. The density of syntactic foam is proportional to the concentration of filler added. The limiting lower densities are determined by the density
of the spheres, the handling requirements of the uncured mix, and the property requirements of the final product. The sphere density also determines its efficiency as a bulking agent; the less dense the spheres, the lower their weight concentration required to achieve a specified composite density [Anderson et al., 1970].

Syntactic foams can be designed and fabricated according to the physical and mechanical property requirements of the application. Depending upon the service conditions, the matrix resin can be chosen from a wide range of thermosetting and thermoplastic resins. Similarly, microspheres of polymer, ceramic or metal can be chosen. Appropriate choice of fillers can produce composites with superior strength, damage tolerance, wear resistance and chemical resistance. The ability to cast a syntactic foam to any desired shape and the ease of machineability of the cured foam make syntactic foams very attractive structural materials [Ferguson and Shaver, 1970].

1.4.5.3 Mechanical properties

Syntactic foams have excellent mechanical properties. They have the ability to absorb considerable amount of energy under compressive loading [Gupta, 2006; Maharsia and Jerro, 2007]. The high specific compressive strength of syntactic foams derives from the resistance of microspheres to compressive loads [Gupta and Woldesenbet, 2003; Gupta and Woldesenbet, 2005; Huang et al., 2006]. The compressive properties of syntactic foams primarily depend on the properties of the microballoons, whereas the tensile properties depend on the matrix material used [Bunn and Mottram, 1993; Gupta and Ricci, 2006]. The microspheres have an extremely strong structure and hence can withstand stresses very well. In the case of two-phase syntactic foam, properties are a function of the properties of the resin and the
microballoon and their proportions. In the case of three-phase syntactic foams, the shape and content of voids play an important role.

A general stress–strain curve for the compression testing of syntactic foams is illustrated in Figure 1.3. A typical characteristic is the appearance of a plateau region, which is marked as "densification region" in the figure. This plateau region corresponds to energy absorption by the material in the process of compression. During the process of crushing, the hollow glass particles tend to fracture and expose the volume enclosed by them. This volume accommodates the material that is getting compressed. Equilibrium between the new volume exposed and volume reduction due to compression is visible in the form of plateau region in the stress–strain curve. When substantial amount of microballoons is broken and the new volume generated is not enough to accommodate the material getting compressed, load again starts increasing as depicted in the figure [Ferguson and Shaver, 1970].

![Figure 1.3 General stress–strain curve for the compression testing of syntactic foam](image)

**Figure 1.3** General stress–strain curve for the compression testing of syntactic foam [Gupta et al., 2001].
1.4.5.4 Low moisture absorption

Another most important property of syntactic foams is their low moisture absorption. Syntactic foams have completely closed cells and therefore, absorb water to a lesser degree compared to foamed plastics in which the cells are open [Gupta et al., 2002; Gupta and Woldesenbet, 2004]. The overall moisture absorption in syntactic foams is affected by the nature of the resin-microsphere interface, and concentration, size and strength of the microsphere. In addition, the chemical and physical properties of filler and binder are also decisive factors [Hobaica and Cook, 1968]. It is reported that for microballoon concentration below 67 vol. %, the water absorption in syntactic foam is independent of density, but above such concentration, the absorptivities increase rapidly due to loss in binder integrity and appearance of cavities [Hobaica and Cook, 1968; Karthikeyan et al., 2001]. Syntactic foams are reported to absorb ~1% water by weight even after immersion in water at room temperature for long periods. Different methods are used to lower the moisture absorption in syntactic foams like addition of hydrophobic compounds to binder (eg. Alkyl alkoxy silane derivatives, amino or epoxy alkoxysilanes etc.) and microsphere dressing (eg. using agents like aminoethoxysilanes) [Shutov, 1991].

1.4.5.5 Isotropic nature

Syntactic foams are isotropic materials due to the randomness of the microstructure; i.e., they tend to behave the same way on every load-bearing axis [Sankaran et al., 2006]. In syntactic foams, the filler is randomly dispersed in the matrix, in a way to obtain a homogeneous and isotropic macroscopic behaviour [Rizzi et al., 2000]. The various properties of syntactic foams do not appear to be associated
with any preferred direction in the material but rather with the orientation of the applied stresses [Mukherjee and Saraf, 1994].

1.4.5.6 Dielectric properties

Syntactic foams are also characterised by low dielectric constants enabling their use in radomes and other products where light weight materials of desired electrical properties are required. By using appropriate inorganic hollow spheres, it is possible to reach very low loss tangents thus avoiding major losses of the radiation energy. Some silica microspheres are characterised by very low dissipation factors making them suitable for development of low-loss syntactic foams. Such foams can be used for radome applications where minimum absorption of electromagnetic energy is required [Puterman et al., 1980].

1.4.5.7 Thermal properties

Thermal properties of syntactic foams are generally dominated by the matrix characteristics. The type of filler also has some effect on the thermal properties of syntactic foams. Syntactic foams are less combustible than their chemically foamed counterparts for the same reason [Shutov, 1991].

1.4.6 Factors affecting the performance of syntactic foams

The properties of syntactic foams are influenced by a number of factors. The most important ones are discussed in this section.

1.4.6.1 Volume fraction of filler

The volume fraction of filler affects the properties of syntactic foams. The density of syntactic foams is inversely proportional to the volume percentage of microballoon. The variation in microballoon concentration affects the mechanical,
dynamic mechanical, thermal and water absorption properties of the syntactic foams. The concentration of filler plays an important role in the processing also. When the microsphere concentration exceeds a certain threshold value, called space factor, the mixture loses its fluidity and changes from a casting composition to a press moulding composition. Each type of microsphere has its own binder: filler ratio at which this transition occurs, marking the boundary between castable and mouldable compositions. The space factor is given by the volume that the microspheres occupy when packed the closest, as given by $K_s = \Phi_{sp} / \Phi_o$, where $\Phi_{sp}$ is the true volume fraction of the spheres, and $\Phi_o$ is the closest packed volume fraction of the spheres [Shutov, 1991].

1.4.6.2 Nature of filler

As discussed in previous sections, the properties of syntactic foams are dependent on nature of microballoon, i.e. material of microballoon, shell thickness, size of microballoon, particle size distribution etc. Different types of microballoons viz. polymeric, glass, carbon, ceramic, metallic etc. can be incorporated in syntactic foams to impart specific properties. In each class of microballoon, different properties can be achieved by suitably selecting chemical constitution of the material of microballoon. The properties of syntactic foams are strongly dependent on the size of the spheres. Larger spheres cause some deterioration of the mechanical properties much more than the small ones [Puterman et al., 1980]. The shell thickness of microballoon is also an important factor affecting the mechanical properties of syntactic foams. For the same volume percentage of microballoon, those with high thickness give syntactic foams of high density. The compressive strength and modulus increase with increase in shell thickness of microballoons [Almeida, 1999; Gupta and Woldesenbet, 2002; Gupta and Woldesenbet, 2002; Gupta et al., 2004; Koopman et al., 2006]. The type of filler used
has some effect on the fire resistance of the syntactic foams. The use of carbon microspheres instead of organic filler makes the foam less combustible [Shutov, 1991].

1.4.6.3 Nature of polymer matrix

For the same volume fraction of the polymer, the properties of syntactic foams are different for different polymers. In the case of thermosetting polymers like epoxy, the curing agent and cure cycle are important parameters [Benderly et al., 2005]. The physical and mechanical properties of syntactic foams thus depend upon their component type and proportions and their structure. Depending on the property requirements, proper binder can be selected. The concentration/nature of the curative/hardener can also be decisive in determining the properties. In some cases, blends of resins may also be used to impart some additional properties [Devi et al., 2007]. The characteristics of typical resins constituting the matrix are described in section 1.2.

1.4.6.4 Quality of the filler-matrix interface

The properties of syntactic foams, particularly the mechanical ones are directly dependent on the filler-binder interface. Microsphere strength had a strong effect on overall compressive properties with interfacial strength playing a secondary, yet significant role. The role of interface is much more critical in the case of tensile and flexural properties. The binder-filler interface plays an important role in moisture absorbing properties also.

1.4.6.5 Method of processing

The method of processing also has a profound influence on the properties of syntactic foams. The properties depend on the method used e.g. casting or moulding.
Syntactic foams made by moulding possess better mechanical properties compared to that prepared by casting. Gupta et al. have reported the effect of processing on the entrapment of voids in both fibre-free and fibre-bearing syntactic foam systems [Gupta et al., 1999].

1.4.7 Types of syntactic foams

The properties of syntactic foams are very much dependent on the nature of polymer matrix employed. Consequently, studies have been focused on exploring different polymer matrices for syntactic foams. Apart from the nature of the matrix, concentration of the matrix, type of curative, type of microballoon etc. are critical parameters in determining the various properties.

1.4.7.1 Epoxy syntactic foams

Epoxy syntactic foams have been the most extensively studied as they can be formulated in a variety of ways to give the desired end product. They are preferred to other matrix systems owing to their high strength and stiffness, thermal and environmental stability, creep resistance and lower shrinkage and water resistance [Li and John, 2008]. Although the high viscosity of epoxy is a disadvantage, the problem can be solved by adopting suitable processing techniques and by selection of the material [Karthikeyan et al., 2000; Karthikeyan et al., 2001]. Bisphenolic, novolac and other structural epoxy resins in combination with different microballoons have been used to process syntactic foams. Epoxy syntactic foams with polystyrene, carbon, mineral microballoons, phenolics (BJO-0930) and glass have been reported [Karthikeyan et al., 2001; Bunn and Mottram, 1993; Gupta et al., 1999]. The properties of epoxy syntactic foams can be tuned by proper choice of the resin system,
blending with other polymer resins and by selecting suitable curative. Epoxy syntactic foams have been widely used in sandwich composites.

The effect of microballoon volume fraction on the properties of epoxy syntactic foams made with microballoons of different density (220, 320, 380, and 460 kg/m$^3$, designated as SF22, SF32, SF38 and SF46 respectively) has been studied by Gupta and Nagornyn. The tensile strength showed a decreasing trend when the microballoon volume percentage was increased from 30 to 60%. All types of syntactic foams showed 60–80% decrease in tensile strength compared to the neat resin. The specific strengths of SF22 and SF32 foams do not show any variation with microballoon concentration in the range of 30–60 vol %. The values showed a decreasing trend for SF38 and SF46 foams, but these values are also closely spaced and the trend can be considered to be nearly constant. The modulus was found to increase with microballoon density [Gupta and Nagornyn, 2006].

Another study conducted by Wouterson et al., for epoxy syntactic foams with three types of microballoons, viz. 3M Scotchlite, K-15 and K-46 glass microballoons, and Phenoset BJO-093 hollow phenolic microballoons, shows that tensile and flexural strength decreased with increasing filler content and was not affected by the component microspheres. The specific tensile strength showed maximum value at 10 vol. % microsphere whereas specific flexural strength decreased with microballoon concentration for all the types of microspheres used (Figure 1.4). The tensile and flexural moduli showed different trends for each type of microspheres with increasing filler content [Wouterson et al., 2005].
The compressive properties of epoxy syntactic foams were reported by Bunn and Mottram. They studied the compressive properties of syntactic foams made from phenolic microballoons with different volume fractions. A decrease in compressive strength was observed on increasing the microballoon volume fraction. The average compressive yield strength ranged from 28 to 71 MPa, and the average initial tangent (compressive modulus of elasticity) ranged from 0.81 to 2.7 GPa as shown in Figure

**Figure 1.4** Specific (a) tensile and (b) flexural properties of epoxy syntactic foam containing (■) K15, (▲) K46 and (●) phenolic microspheres [Wouterson et al., 2005]
1.5. Thus, the compressive yield strength and initial modulus were linearly dependent on the bulk density and the volume fraction of microballoons [Bunn and Mottram, 1993]. Palumbo et al. also observed a reduction in compressive strength from 70 MPa to 50 MPa as the weight fraction of the microballoons increased from 15% to 35% [Palumbo et al., 1996]. Zihlif and Ragosta found that the density, elastic modulus, compressive yield stress and strain decreased with increase in the volume fraction of microballoons [Zihlif and Ragosta, 2001].

![Graphs showing the variation of compressive strength and modulus with bulk density of epoxy syntactic foams](image_url)

**Figure 1.5** Variation of (a) compressive strength and (b) modulus with bulk density of epoxy syntactic foams [Bunn and Mottram, 1993]
Studies by Wouterson et al. show that the specific compressive yield strength decreased with increasing filler content for epoxy syntactic foams with phenolic and K-15 (glass) microspheres. However, an upward trend is observed for the syntactic foams with K-46 microspheres, which is attributed to a relatively minor decrease in the compressive yield strength compared to the decrease in density. The difference in compressive strength of the syntactic foams with K-15 and K-46 microspheres shows the influence of compressive strength on the wall thickness of microspheres. The specific compressive modulus increased with microballoon concentration for syntactic foams with K-15 and K-46, whereas in the case of phenolic microballoon based syntactic foams, the modulus remains almost constant with microballoon concentration [Wouterson et al., 2005]. The compressive strength and modulus of epoxy syntactic foams are found to be higher for those processed using microballoons of higher shell thickness [Wouterson et al., 2005; Gupta and Woldesenbet, 2002; Gupta and Woldesenbet, 2004; Almeida, 1999]. The approach of changing the microballoon thickness, keeping the microballoon composition constant is more effective than changing the microballoon volume fraction to change the syntactic foam density as it considerably increases the specific strength [Gupta and Woldesenbet, 2004].

Studies on moisture absorption of syntactic foams reveal that S22 (glass microballoon, density=220kg/m$^3$) type syntactic foam absorbed 6.7% and 2.5% moisture in deionised (DI) and salt water, respectively whereas K-46 (glass microballoon, density=460kg/m$^3$) syntactic foam absorbed 3.9% and 1.9% respectively (Figure 1.6). Considerable decrease in compressive modulus is observed in wet samples compared to the dry samples of the same type. For S22 type syntactic foam, the decrease is 49, 51, 65 and 68 % respectively for low temperature DI water, low temperature salt water, high temperature DI water and high temperature salt water. The
corresponding decrease in the case of K-46 syntactic foams is measured to be 48, 64, 57 and 60% respectively. No significant difference is observed in the peak compressive strength of low temperature specimens compared to the dry specimens. However, high temperature specimens showed 36, 33, 34 and 31% decrease in compressive strength for S22 DI water, S22 salt water, K-46 DI water and K-46 salt water immersed samples compared to the corresponding dry samples [Gupta and Woldesenbet, 2003].

![Figure 1.6 Moisture absorption of epoxy syntactic foams at room temperature and 70°C](image)

The fracture toughness of epoxy syntactic foams with glass microballoons of densities 220, 320, 380, and 460 kg/m$^3$ decreased from 2 MPa.m$^{0.5}$ to 0.6 MPa.m$^{0.5}$ as the volume percentage of microballoon increased from 30% to 65% (Figure 1.7). The decrease in fracture toughness was more (30%) as the volume percentage of the microballoons increased from 60% to 65% [Gorugantu, 2005]. The fracture toughness of epoxy syntactic foams of lower microballoon concentrations i.e. 0% to 20%, shows an increasing trend with increasing volume fraction of microballoons. This is attributed
to crack front bowing mechanisms which assumes that the microspheres can resist crack propagation and cause crack front to bow out between the microspheres. High density microballoons contribute to higher strength and stiffness in addition to crack bowing mechanisms, due to higher strength of the filler [Wouterson et al., 2004]. These two studies show that there might exist an optimum volume fraction of microballoons at which the fracture toughness reaches a maximum. The fracture toughness and the fracture energy did not vary significantly with change in temperature in the range of 50 to 125°C [Zihlif and Ragosta, 2001].

![Figure 1.7: Variation of fracture toughness with increase in density of microballoons [Gorugantu, 2005]](image)

By changing the resin and curing agent, fracture toughness of epoxy (Epon 815) syntactic foams has been shown to be improved without sacrificing the mechanical and thermal properties. For syntactic foams in which epoxy is cured by anhydride, the addition of elastomer improved the fracture toughness while flexural strength was unaffected. For the cycloaliphatic amine-cured system, the addition of elastomer did not affect the fracture toughness. The use of cycloamine curing agent rather than anhydride curing agent yielded a 30% increase in fracture toughness due to better curing properties [Benderly et al., 2005].
Dynamic mechanical analysis of epoxy syntactic foams shows higher glass transition temperature for the syntactic foams compared to the neat resin due to the reinforcing effect of the microballoons that affects the mobility of the polymeric chains in the interphase region between the matrix and the microballoons. The reduction in modulus values with increasing temperature is much lower in syntactic foams compared to neat resin. The room temperature tan δ values of the syntactic foams showed a relatively large decrease compared to the neat resin, due to the presence of rigid glass microballoons that too at high concentration levels [Sankaran et al., 2006].

The coefficient of thermal expansion (CTE) of epoxy syntactic foams is lower than that of neat epoxy. The CTE of epoxy syntactic foam with carbon microsphere decreases as the filler concentration increases. The CTE values for foams with 0 (pure binder), 15, 20, and 25 vol% filler are 55x10^{-6}, 45 x10^{-6}, 37 x10^{-6}, and 13 x10^{-6} °C^{-1}, respectively. These values do not change for temperatures up to 370°C, which is important for materials used as thermal insulation where the heat loads can vary abruptly [Shutov, 1986]. The dielectric constant was decreased with increase in frequency and filler content [Park et al., 2005].

1.4.7.2 Phenolic syntactic foams

Syntactic foams based on phenolic resins are very popular in aerospace area as they can serve the purpose of low-density ablatives. They have low thermal diffusivity and high char forming properties which are desirable for a good ablative. Phenolic syntactic foams and composites have become well established in the offshore oil and gas industry over the past few years as highly fire resistant, thermally insulative coatings and structures. Phenolic syntactic foams have good resistance to burning and have improved thermal stability at 300°C. The undesirable friable character of phenolic
foams can be markedly improved by the introduction of microballoon [Okuno and Woodhams, 1974]. Syntactic foams based on phenolic binder (novolac) is having lower CTE \(7 \times 10^{-6} \, {^\circ}C^{-1}\) for an apparent density of 200-300 kg/m^3) compared to epoxy based system [Shutov, 1986]. Phenolic syntactic foams based on silas microballoon, IG-101 (glass microballoons), amino microballoons, fly ash etc. have been reported [Argade et al., 2004; Huang et al., 2006; Okuno and Woodhams, 1974]. For syntactic foams prepared from blends of six phenolic resins and carbon microbubbles, the compressive strength of the phenolic resin foam is equivalent to the strength of foams made from a polyimide resin [McIlroy, 1980].

Polybenzoxazines are also explored in syntactic foams. In the case of polybenzoxazine syntactic foams, tensile and compressive properties were optimised at about 68% by volume of microballoon while flexural strength decreased marginally on increasing the microballoon content. Although the specific tensile and compressive strength showed a maximum followed by a decrease, the specific flexural strength systematically increased with microballoon content (Figure 1.8). Since polybenzoxazine is basically a phenolic resin, these composites could be a potential candidate for lightweight thermostructural applications as in ablative thermal insulation [Kumar et al., 2008].

1.4.7.3 Polyimide syntactic foams

Polyimide syntactic foams made with silica microballoons have good electrical as well as mechanical properties. They have been used for encapsulation of electrical devices [Calahorra et al., 1987]. They are remarkably stable mechanically at elevated temperatures. For eg. HTF-60 (apparent density=370kg/m^3), a type of polyimide syntactic foam, loses only less than 20% of its initial strength as the temperature rises
from 200°C to 370°C. These syntactic foams can remain intact under compressive strains, $\varepsilon$, up to 40% at 370°C, while under tension at the same temperature, fractures at $\varepsilon=1.8\%$ with a tensile strength of 3.2 MPa. The material loses 10% of its weight when heated to 528°C in air, or to 557°C in an inert atmosphere. The limitations of the material are that it shrinks on curing by up to 20%, and curing takes a long time, with the evolution of toxic and flammable gases (acetic acid, acetic anhydride, NMP etc.). Polybenzimidazole foam with phenolic or glass microspheres also has good thermal properties. They are not combustible (starting to lose weight at 600°C) and can retain good mechanical properties up to 350°C [Shutov, 1986].

![Figure 1.8 Variation of specific mechanical strength of polybenzoxazine syntactic foams with microballoon content](Kumar et al., 2008)

Due to the presence of porous structure, moisture may degrade the electrical properties of polyimide syntactic foams. To reduce moisture absorption, the syntactic foams were made using silica microballoons having parylene (di-(chloro-para-xylylene)) coating. Moisture absorption by the coated syntactic foam at 95% R.H. at 50°C was found to be 5% by weight after 60 days exposure. Parylene coating provides
an efficient water vapour barrier to the three-phase syntactic foam [Calahorra et al., 1987].

The polyimide syntactic foam, HTF-60, with the formulation, RC-5081 (polyimide solids), B35A glass bubbles, acetic anhydride and 4-benzoylpyridine, has been proven to be a tough system capable of being compressed to over 40% strain without catastrophic failure. The combination of the polyimide and glass microballoons has shown excellent retention of strength at elevated temperatures. The improvement in strength retention of HTF-60 over the sintered polyimide is due to the high percentage of microballoons in HTF-60 [Rand, 1973].

1.4.7.4 Polyurethane syntactic foams

Polyurethanes are also used in syntactic foams and are mainly used for packaging applications [Adrien et al., 2007; Rittel, 2005]. U.S. Patent No. 4,916,173 discloses polyurethane syntactic foam compositions which have high glass transition temperatures and low coefficient of thermal expansion. A typical polyurethane composition consists of a blend of (a) 30-55% of a polyisocyanate, (b) 9-35% of an amine-based polyol, (c) 5-40% of a polyether triol, (d) 3-10% of a molecular sieve and (e) 10-40% of a hollow microsphere filler (all percentages being by weight of the total composition). The molecular sieve functions as a moisture scavenger which reduces foaming in the moulding process and yields a product of uniform density whereas polyols provide high glass transition temperatures and proper reactivity. The materials show improved mechanical strength to permit their use under autoclave pressures and temperatures [Otloski and Sollner, 1990].

Another US Patent, No. 6,706,776, details polyurethane syntactic foams which are hydrolytically stable and have a high compression modulus (greater than 2068...
MPa). These syntactic foams can be exposed to water at temperatures from 0 to 40°C for up to 10 years without degradation. They exhibit a long pot-life and short demoulding times (less than 10 minutes). In particular, at about the same hardness and density, a liquid diphenylmethane diisocyanate vs. polymethylene poly (phenylisocyanate) in combination with a low unsaturation difunctional polyether polyl, the resultant syntactic foams have higher tensile strength and elongation (about 50% more), higher tear strength (about 3 times higher), lower Taber abrasion (30 to 50% less), and considerably lower water absorption (25 to 50% less in fresh water, and 20 to 30% less in salt water) [Markush et al., 2004].

A polyurethane syntactic foam with a combination of low-density, strength, fluidity and flame retardancy was obtained by mixing an organic polyl, a polyisocyanate, a catalyst for the reaction of the polyl and polyisocyanate, microballoons and a flame retardant. An example of the flame retardant is tris (2-chloroethyl) phosphate. A combination of the polyl and polyisocyanate are liquid at 25°C and the amount of microballoons present are sufficient to provide a non-castable mixture in the absence of the flame retardant and the amount of flame retardant is sufficient to provide a castable mixture which will flow in a mould cavity. These syntactic foams are claimed to be suitable for structural purposes, such as replacement for wood and have the added advantage of being flame retardant [Harper, 1978].

1.4.7.5 Polyester syntactic foams

The polyesters are room temperature cured with shrinkage, cracking, and exotherm being the major problems. Polyester syntactic foams have been used for floating devices. The low cost of the polyester systems has dictated their use in syntactic foams in large applications such as submarine structural void fillers [Hobaica
and Cook, 1968]. It has been revealed that the hollow-sphere fraction of the fly-ash from the Banhida Power-Station, Hungary was suitable for preparation of polyester syntactic foams without any further purification or refinement [Hirschberg et al., 1987].

Silane coupling agent has been shown to improve both performance and versatility of floating devices based on polyester syntactic foams. It improves the bond between the glass microballoons and the polyester resin, thereby making the spheres stronger without increasing their wall thickness. The use of coupling agent also improves the flow of the material during moulding, resulting in fewer trapped air bubbles. Otherwise, these bubbles could produce stress in the wall of the sphere. The silane material, representing only 1% of total filler weight, forms bonds at the interface between the organic resin and the inorganic microballoons. This produces a strong composite and improves strength retention, particularly in wet environments [Elastomerics, 1980].

1.4.7.6 Silicone syntactic foams

Silicone resins with their very attractive dielectric properties are very promising thermosetting resins for electromagnetic applications. They have been used as a matrix material in composites based on glass or quartz fibres for high performance radomes. However, the use of silicone resins for syntactic foams has not been largely studied. For processing a silicone syntactic foam based on phenyl methyl polysiloxane, powdered silicone resin was first processed in a ball-mill and then dry-blended with the silica microballoon. The catalyst and curing agents were added to the resin prior to milling. Curing was carried out in a constant volume mould at a maximum temperature of 200°C and pressure of 206 MPa for 15-20 minutes. The compressive properties were studied using different catalyst combinations of dibutyl tin dilaurate (DBTDL), tin
octoate (TO) and triethanolamine (TEA). The combination of TO and TEA results in better compressive properties, especially at the lower densities [Kenig et al., 1984].

Glass microballoon filled polydimethyl siloxane (PDMS), which is cross-linked at room temperature using methyl tris methyl ethyl ketoxime silane in presence of DBTDL catalyst, was demonstrated to show tunable mechanical properties depending on the resin-to-filler ratio. Though the mechanical properties diminished on adding microballoon, the specific mechanical properties improved on embedding microballoons. The specific heat showed a decreasing trend with increase in microballoon concentration. The thermal conductivity also got reduced by the incorporation of silica microballoons. This low density system can withstand temperatures up to 700K and can find extensive space applications [Sukumaran et al., 2009].

1.4.7.7 Elastomeric syntactic foams

Elastomeric syntactic foams were developed for use as stress relief coatings on encapsulated electronic components. The high moduli and the ability to relieve high stresses make syntactic foams ideal for this application. These foams have been made with urethane, silicone, and polysulfide elastomers blended with glass and phenolic microballoons. The polysulfide/phenolic microballoon foam has good pot life and can be diluted with toluene to ease processing. It is useful for high voltage applications where a good bond is required. The variety of compressive properties that are made available by varying the elastomer, microbubble, and the formulation has provided a useful engineering material that can be easily formulated for particular application. The urethane elastomer/glass microbubble foam is a relatively high strength material which is difficult to process because of its high viscosity and short pot life. The silicone/glass
microbubble foam is made with a low viscosity resin which has a long pot life [Rand, 1978].

1.4.7.8 Nylon syntactic foams

Nylon syntactic foams made with phenolic microballoons are proposed for use in the nose cap of Scout re-entry vehicle produced by Langley Research Centre. The formulation of the ablative material is 40% by weight of Nylon 66, 35% by weight of phenolic microspheres, 25% by weight of phenolic novolac resin. The syntactic foam exhibited several deficiencies as a plastic material, like low mechanical properties, high porosity, difficult processing, heterogeneous microstructure, and variability of raw materials [Keller, 1968].

1.4.7.9 Polybutadiene syntactic foams

Syntactic foams based on polybutadiene matrix, whose microstructure contains less than 80% of 1, 2-units providing better control of the exothermicity during the curing of the resin, are of particular importance when manufacturing articles of great size like floating members. The microspheres may be of borosilicate glass, silica, carbon, or thermoplastic or thermoset resins, whose diameter is generally from 10 to 500 µm, and the "macrospheres" are of glass, or of thermoplastic or thermoset resins, whose diameter is in most cases from 1 to 100 mm. Generally, the microballoon concentration is 5 to 50 phr [Dawans, 1978].

1.4.7.10 Polypropylene syntactic foams

Syntactic foams based on polypropylene also have been studied. The use of glass microballoons is suitable for obtaining low-density polypropylene syntactic foam without great loss in mechanical properties. The hollow space in polypropylene
syntactic foams may also improve the thermal insulating properties, in addition to isotropy and better surface finishing [Ana et al., 2002].

Shell chemicals UK Ltd., developed a polypropylene syntactic foam (carizite) that can be extruded or injection moulded. It contains tiny glass spheres (<50µm in diameter) that can withstand extreme pressures. Carizite has been used for insulating oil transmission pipe in North Sea. Its processability, extremely high compressive strength, and very low shrinkage make it a candidate for structural composites in automotive applications and the like. Carizite has a density of 680 kg/m$^3$, compressive strength of 33 MPa, ultimate tensile strength of 10.5 MPa, and dimensional stability of 0.2% at 70°C [Modern Plastics International, 1994].

1.4.7.11 Carbon-Carbon syntactic foams

Carbon-carbon syntactic foam consists of hollow carbon microspheres bounded by carbonaceous matter. It has high specific strength coupled with useful thermal insulating properties and is especially useful for high temperature applications [Gebhardt and Juneau, 1984]. Carbon microspheres of various types, particle size, and wall thickness, along with different carbonaceous binder materials, solvents, and moulding pressures are used for C-C syntactic foams [Benton and Schmitt, 1972].

Bruneton et al. has detailed the processing of C-C syntactic foams. The precursor of the microspheres is phenolic resin. When the resin gets heated up, it transforms into a liquid or viscous product. Bubbles are produced by the evolution of volatile products. By controlling the heating rate, the starting material gets converted into hollow individual spheres. The diameter of the spheres varies between some micrometers to several tens of micrometers, and shell thickness varies from 1 to 5
micrometers. The matrix is also phenolic resin. Phenolic resin and the microspheres are soaked in solvent, which dissolves the resin and disperses the spheres. The mixture is moulded and excess resin as well as the solvent is removed. The resulting material is polymerised and then carbonised at a temperature close to 1000°C. The density of the resulting foam was 300 kg/m$^3$ [Bruneton et al., 2002]. It has been shown that the use of the resin-starch binder significantly increases the plasticity of the foam during the carbonisation step to minimise deleterious internal stressing [Malthouse and Masters, 1974].

1.4.8 Recent advances in syntactic foams

Syntactic foams have been used in a wide range of applications. Due to the wide range of possible applications, it is desirable to modify the properties of syntactic foams as per the requirements. Recently, a lot of studies have been focused on improving the properties of syntactic foams. Various types of filler materials have been used to modify the foam microstructure/properties to attain certain desired properties.

1.4.8.1 Fibre reinforced syntactic foams

Several works have been devoted to improving the performance of syntactic foams by fibre reinforcement [Huang et al., 2006; Karthikeyan et al., 2000; Karthikeyan et al. 2001; Karthikeyan et al., 2004; Karthikeyan et al. 2005]. Syntactic foams reinforced with fibre are better core for application in sandwich composites.

The method of processing and fibre composition has profound influence on the properties of syntactic foams. Karthikeyan et al. studied the mechanical properties of fibre reinforced syntactic foams containing 0.9, 1.76, 2.54, 3.54 and 4.5 vol% fibre. Syntactic foam with 3.54 % fibre was processed in two different ways. In the first
method, microballoons were added to resin prior to fibre. In the second method, the fibres were added first, followed by microballoons. The results show that the flexural modulus increased with fibre content, with the exception of 1.76% and 3.54% (processed by first method) of fibres. This deviation was due to a higher void content for 1.76% fibre system and a non-uniform distribution of fibres for 3.5% fibre system. The difference in fibre distribution in the case of 3.54% fibre system was because the fibres were unable to distribute themselves in a medium which contains microballoons dispersed in a resin. Thus, the latter method was found to be more effective as evident from the lower void content and good mechanical properties [Karthikeyan et al., 2000; Karthikeyan et al. 2005].

Wouterson et al. also observed an increase in the ultimate tensile strength and Young's modulus with increasing fibre loading, for epoxy (Epicote 1006) syntactic foams with hollow phenolic microspheres (Phenoset BJO-093). The ultimate tensile strength increased by 40% and Young's modulus by 115%, with the addition of 3 wt% short carbon fibre (SCF). For the Young's modulus, a linear additive trend with the increase in SCF weight fraction was observed [Wouterson et al., 2007]

Karthikeyan et al. found that compressive modulus and specific compressive modulus increased with increase in fibre concentration, despite the presence of voids. The increase in compressive properties is due to the increased load-bearing ability of the fibrous reinforcements [Karthikeyan et al., 2004]. In another study, Karthikeyan et al. observed that fibre free syntactic foams had a higher compressive strength than the fibre-bearing one whereas the moduli values did not differ much. The difference in strength is correlated with the amount of voids present in the two foams [Karthikeyan et al., 2000].
The compressive strength of the fibre reinforced syntactic foams after immersion in aqueous media consisting of either saline or seawater shows that the strength decreased in samples exposed to water vapour, but the saline or seawater immersed samples showed higher compressive strength when compared to the dry sample. The decrease in strength in the water vapour-exposed case is ascribed to higher absorption of water and to debonding and damaging of interfaces. The enhanced strength values for the samples immersed in saltish media is due to the larger size of the chloride ion and resultant changes in the stress state around the fibre-bearing regions \cite{Karthikeyan et al., 2001}.

Huang et al. studied phenolic syntactic foams with amino microspheres reinforced with aramid (Kevlar-49, length=ca.12mm) and carbon (C-30, length=ca.24mm) fibres. The composition of the syntactic foams has been kept constant (4 wt% fibre, 19 wt% phenolic resin, and 77 wt% amino microspheres). It was observed that fibre length had only a minor effect on compressive strength of the syntactic foams. Fibre length and orientations had major effects on shear properties in some foams. Higher moduli values were reported for long fibre-based foams (24 mm) compared to shorter fibre based foams (12mm) \cite{Huang et al., 2006}.

The fracture toughness, $K_{IC}$, and critical energy release rate, $G_{IC}$, increased by 95% and 90%, respectively, upon introduction of 3 wt% short carbon fibre (SCF) in epoxy (Epicote 1600) syntactic foam, indicating the potent toughening potential for SCF in syntactic foam systems. The specific energy required to create new surfaces was enhanced by the presence of fibres and was the main contributor to the toughness of the short fibre reinforced syntactic foam (SFRSF) \cite{Wouterson et al., 2007}.
A study on thermal stability of short fibre reinforced syntactic foams (SFRSF) shows that thermal stability is independent of the fibre length and fibre weight fractions. The thermal stability of SFRSF is primarily governed by the matrix of the SFRSF. Storage modulus increased with the short fibre content (Figure 1.9 (a)). Despite a slight increase in the glass transition temperature, $T_g$, compared to neat syntactic foam, the variations in fibre content and fibre length do not affect the $T_g$ of SFRSF (Figure 1.9 (b)) [Wouterson et al., 2007].

The effect of microballoon addition on the properties of silica fibre reinforced polybenzoxazines has been reported. Specific tensile strength enhanced upon inclusion of microspheres up to about 47% by volume of microballoon, beyond which, a decreasing trend was observed. Specific compressive strength also followed a similar trend. Specific flexural strength decreased marginally and practically stagnated beyond 57 vol. % of microspheres. A composition with about 55 vol. % of microballoon is good enough for moderate load bearing thermostructural applications (low density moderate strength materials) without great penalty on mass [Kumar et al., 2008].

1.4.8.2 Nanoclay incorporated syntactic foams

Nanoclay has been used to improve the properties of syntactic foams. The improvement in performance is attributed to the unique phase morphology and better interfacial properties of the resulting composites. In conventional composites, phase mixing occurs on a macroscopic scale, whereas in nanocomposites, phase mixing occurs on a nanometre length scale. A large number of interfaces are created in a nanocomposite upon dispersion of nanoparticles, which leads to increase in strength of the composite. In general, incorporation of nanoclay improves the strength, fracture strain and damage tolerance properties of syntactic foams without significantly
affecting the density of syntactic foams. The highly damage tolerant hybrid foams will be useful as core in sandwich composites for various applications.

Figure 1.9 The variation of (a) storage modulus and (b) tan δ with temperature for short carbon fibre-reinforced syntactic foam with different fibre weight fractions and fibre lengths [Wouterson et al., 2007]

Maharsia et al. observed an increase in tensile strength of epoxy syntactic foam with nanoclay addition, attributed to the presence of exfoliated/intercalated nanoclay particles which restrict the mobility of polymer chains during tensile loading [Maharsia
and Jerro, 2007]. Studies done by Wouterson et al. shows a 13% reduction in tensile strength and 19.5% improvement in Young's modulus by the introduction of 2 wt% of nanoclay to epoxy syntactic foam. The reduction in tensile strength was attributed to the presence of voids and agglomeration of the nanoclay layers. The tensile properties of these nanoclay reinforced syntactic foam were not as good as those observed for short fibre-reinforced syntactic foams [Wouterson et al., 2007].

Addition of 2% nanoclay particles to epoxy syntactic foam has resulted in an overall reduction in flexural strength of the syntactic foams by around 11% whereas addition of 5% nanoclay increased the strength of low density syntactic foams (with microballoons of lower shell thickness) by around 22%, with no considerable difference in the strength of nanoclay syntactic foams containing microballoons of higher shell thickness [Maharsia et al., 2006]. Flexural toughness, which is measured as the area under stress-strain curve, increased upon the addition of 5% nanoclay particles. However, the toughness showed a decrease upon the addition of 2% nanoclay particles [Maharsia, 2005].

Another study conducted by Maharsia et al. shows that epoxy syntactic foams containing 2% nanoclay particles have 10-20% lower compressive strength in comparison to plain syntactic foams. The strength of 5% nanoclay containing foams is higher than corresponding bare syntactic foams except in the case of syntactic foams with microballoons of density, 380kg/m$^3$ and 460kg/m$^3$. The toughness of the material, measured as the area under stress strain curve, is found to increase by 80-200% [Maharsia and Jerro, 2005].

The fracture toughness, $K_{IC}$, and critical energy release rate, $G_{IC}$, of nanoclay reinforced epoxy syntactic foams have been reported. For the foams containing 1–2
wt% nanoclay particles, an increase in $K_{IC}$ is observed compared to pristine syntactic foam. The $K_{IC}$ value slightly drops for specimens containing more than 1 wt% nanoclay due to increased agglomeration of the nanoclay layers. The trend in $G_{IC}$ vs. wt% nanoclay is similar to the trend observed for $K_{IC}$. Introduction of up to 0.75 wt% nanoclay causes a 41% reduction in $G_{IC}$. $G_{IC}$ shows a significant increase of 104% for specimens containing 1 wt% nanoclay, compared to bare syntactic foams. The increase in both $K_{IC}$ and $G_{IC}$ for syntactic foams containing 1 wt% nanoclay indicates the excellent toughening potential of nanoclay in syntactic foams [Wouterson et al., 2007].

A comparison of the fracture properties of nanoclay reinforced syntactic foam (NCRSF) and short fibre reinforced syntactic foam (SFRSF) is depicted in Figure 1.10.

![Figure 1.10](image)

**Figure 1.10** Comparison of the fracture properties of nanoclay reinforced syntactic foam and short fibre reinforced syntactic foam as a function of reinforcement concentration [Wouterson et al., 2007].

### 1.4.8.3 Rubberised syntactic foams

Epoxy systems which are extensively used in syntactic foams tend to be brittle due to high cross-link density. Therefore, the impact tolerance of epoxy-based foam is weak
and the residual strength is low. Addition of rubber particles provides an effective way to modify the matrix of syntactic foams for achieving better impact and fracture toughening properties. The rubber particles absorb more impact energy through elastic deformation of the particles which leads to a higher toughness of the matrix. Also, the low stiffness rubber particles serve as stress concentrators. When the stress exceeds the strength of the material, microcracks will initiate, consuming considerable amount of impact energy and resulting in higher energy absorption capacity. The propagation of microcracks will be blunted, stopped, and arrested by the rubber particles through mechanisms like rubber pinning and rubber bridging-over. Therefore, the addition of rubber particles is an effective method for absorbing impact energy. Damage tolerant hybrid foams based on rubberised syntactic foams will be useful for aerospace and marine structures [Maharsia, 2005; Gupta, 2005; Li and John, 2008; Maharsia et al., 2006].

### 1.4.8.4 Functionally graded syntactic foams

Functionally graded syntactic foams (FGSFs) can be obtained by creating a gradient of microballoon volume fraction (VF-type) or thickness (RR-type) along the length or thickness of the syntactic foam to achieve variation in density and mechanical properties. The schematic representation of both VF-type and RR-type FGSFs are shown in Figure 1.11. VF-type systems have disadvantages like possibility of warping or localised swelling if it is exposed to varying temperature and moisture conditions, due to the difference in resin concentration along the length or thickness. The approach also poses severe limitations on the minimum density achievable in such materials, particularly when the filler particles have lower density than the matrix resin. It can also lead to premature fracture due to non uniform distribution of stress along the
microballoon gradient and existence of resin/microballoon rich sides in the material. In the case of RR-type, volume fraction is available as an additional parameter for controlling the properties of the FGSF [Gupta and Ricci, 2006; Gupta, 2007; Gupta et al., 2008]

![Figure 1.11 Schematic representations of (a) VF-type and (b) RR-type functionally gradient syntactic foams [Gupta and Ricci, 2006]](image)

**Figure 1.11** Schematic representations of (a) VF-type and (b) RR-type functionally gradient syntactic foams [Gupta and Ricci, 2006]

**1.4.8.5 Sandwich composites with syntactic foam as core**

Syntactic foams have been used as core in sandwich composites due to their higher compressive strength, damage tolerance, low moisture absorption, high structural efficiency and good thermal insulation. Unlike honey comb core sandwich composites, where the interfacial strength between the skins and core is critical due to the failure originating mainly at such places, the strength of syntactic foam core sandwich composites assumes importance since the material can fail at any point (interface or foam core) [Gupta, 2003; Gupta and Sankaran, 1999; bWoldesenbet et al., 2005]

Since the porosity in syntactic foams is in closed form, they provide relatively smoother surface compared to open-cell structured foams. The closed cell structure
provides continuous contact between the skin and the core materials and thus makes interfacial strength better compared to other cores, such as open-cell structured foams. In the case of open-cell structured foams, due to the presence of open porosity, the depressions on the surface leads to point contact between the skin and the core while forming the sandwich structures. Therefore, near-planar contact between skin and core can be achieved if syntactic foam is used as core material thereby providing uniform stress distribution on the surface in the sandwich structure and superior bonding between skin and core compared to other polymeric foams. Lamination of the skins can be done directly over the core material to ensure integral bonding between skin and core. The ability of syntactic foams to keep the damages highly localised, especially in sandwich constructions has led to the development of damage-tolerant designs [Gupta et al., 2002]

Low moisture absorption is another advantage of using syntactic foams as core material. Even if the skin material is damaged and the core is exposed to the external environment, moisture absorption by the structure remains limited. In the case of open-cell-structured foams and honey comb structured cores, any damage to the skins may lead to considerable moisture absorption that can cause hygrothermal degradation and structural instability. The advantages such as low moisture absorption and continuous contact between the core and the skins coupled with high damage tolerance and low density have made possible the wide spread use of syntactic foams as the core material for sandwich composites [Woldesenbet et al., 2005].

1.4.8.6 Cement based syntactic foams

Cement based syntactic foams have been recently introduced by Li et al. This type of syntactic foam is a multi-phase composite material with microballoons dispersed
in a rubber latex toughened cement paste matrix. Other phases of these composites contain trace amounts of nanofibre and nanoclay. Cement based syntactic foam has a higher capacity for dissipating impact energy without affecting the strength as compared to the control cement paste core. Compared to a polymer based foam core having similar compositions, cement based foam has a comparable energy dissipation capacity. The rubber latex toughens the cement matrix and stores more elastic strain energy. The microballoons reduce the weight, retain water tightness and provide micro-length scale mechanisms for energy absorption. The nanoclay improves the crystal structure of the cement hydrates. Microballoon and microfibre increase the number of sites for energy absorption through microballoon crushing, microballoon/matrix interfacial debonding, matrix microcracking, and fibre pull-out. Figure 1.12 shows the fractured surface of a cement-based syntactic foam where microballoon crushing, interfacial debonding, and fibre pull-out can be seen [Li and Muthyala, 2008].

![Figure 1.12](image.png)

**Figure 1.12** *Micro length-scale mechanisms for energy absorption in cement based syntactic foam [Li and Muthyala, 2008]*

### 1.4.9 Applications of syntactic foams

Syntactic foams offer an outstanding combination of properties when compared to conventional cellular foams and bulk materials. They can be easily moulded and
machined into various desired shapes as per requirements of the applications. The possibilities of making wide range of densities are the key to these materials gaining increasing attention. In general, syntactic foams find increasingly diverse applications, ranging from packaging materials for expensive components to core material in sandwich structures used in automobile, aerospace, transportation and deep sea submersibles.

1.4.9.1 Buoyancy applications

The most important application of syntactic foams is in deep-submergence buoyancy where the compressive properties and low moisture-absorption properties are of prime importance [Ferguson and Shaver, 1970]. They have been used as the principal source of supplementary buoyancy in recently developed deep submergence vehicles. Glass microballoon based syntactic foams are particularly used for this application due to their high compressive strength [Calahorra et al., 1987]. The combined effect of increased hydrostatic pressure, temperature and water ingress found in ultra deep water places a greater demand on syntactic foams.

Syntactic foams have been a highly buoyant structural material for open-frame, remotely operated vehicles (ROVs) [Hinves and Douglas, 1993]. In the area of naval and marine engineering, syntactic foams have been used for structural elements such as hulls, ribs and decks, for components at deep depth such as submarines, submerged buoys, deep sea platforms and pipe joints, and for shielding and repairing submerged apparatuses [Rizzi et al., 2000].

Oceanographers depend on syntactic foams to suspend instrumentation in deep ocean studies [Oil and Gas Journal, 1988]. Syntactic foams have been suggested as a
foamed jacketing compound for a buoyant underwater communication cable for the US
Navy [Trainer et al., 2000].

1.4.9.2 Thermal insulation material

Syntactic foams have been used as thermal insulation material for deepwater sub
sea equipments and pipelines. The hollow spherical particles in syntactic foams
encapsulate the insulating gas protecting the insulation from collapse due to the high
pressures encountered in the subsea environment [Plummer et al., 2001]. Components
that are typically insulated include wet trees and valves, jumpers, sleds and pipeline-end
manifolds, risers and flowlines [Watkins and Hershey, 2001].

A new underwater thermal insulation has been designed, which is a hybrid
composite of two constituents, a syntactic foam and an insulating aerogel blanket
[Bardy et al., 2006]. Syntactic foams have been identified as suitable insulating
materials for pipelines used in offshore exploration and conveying of oil and gas
resources in deep water [Fine et al., 2003; Watkins and Hershey, 1993].

1.4.9.3 In Aerospace industry

There is an increasing demand for syntactic foams in aerospace industry.
Depending on the resin system used, syntactic foam has the potential for an improved
transition temperature and a low dielectric constant, making it ideal for space use.
Syntactic foams are good potting compounds, and have been used in aerospace industry
as fillers for finishing holes and edges in honeycomb structures. For thin panels, they
may be specified for entire sandwich cores.

Westland Aerospace, Isle of Wright, has used syntactic foam plugs for a number
of years. Here, the syntactic foam consists of small, hollow, phenolic-type spheres in a
thermosetting resin binder (mineral-filled paste epoxy, a plasticised liquid epoxy and an appropriate hardener). This syntactic foam has very high compressive yield strength for a number of applications [Bunn and Mottram, 1993; Wang and Watkins, 2003].

Epoxy- and phenolic-based syntactic foams have been successfully used for thermal protection of atmospheric re-entry space vehicles and to prevent structures from the extreme heat flux of rocket exhaust plumes. Phenolic syntactic foams have low thermal diffusivity and high char forming properties which are desirable for a good ablative. Moreover, syntactic foams are strong enough to encounter the aerodynamic shear and have adequate mass saving advantage. The thermal protection systems having low density as syntactic foams are advantageous in reducing weight of total payload, or the lift-off weight of the launch vehicle. The Pathfinder used a phenolic honeycomb filled with a cork and silica bead filled epoxy, SLA-561, for the Mars entry heat shield [Guthrie et al., 2000]. Syntactic foam based light weight polymer composites have been successfully used in thermal protection of atmospheric re-entry spacecrafts such as ARD (ESA), Appollo (NASA) and Shenshou (China). While ARD and Apollo used phenolic resin as binder, Shenshou is reported to have used silicone for the purpose. In fact, for extreme heat flux conditions, ablative based thermal protection system is the only way to dissipate the heat and protect the space vehicle. Low density fillers offer low thermal diffusivity apart from low mass-fraction for the thermal protection system (TPS).

An epoxy-based composite nose cap has been developed for the space shuttle solid rocket boosters (SRBs) which consists of a core of epoxy-based syntactic foam (3M SC350G) sandwiched between composite laminates (Hexcel's AGP370-8H/3501-6) [Stuckey et al., 2001]. Special formulations of syntactic foam are used by NASA to
insulate the fuel tanks and solid rocket boosters of the Space Shuttle [Syntactic Foam adds Strength and Buoyancy].

A "spray-on" syntactic foam insulation that does not crack from repeated thermal cycling has been suggested for cryogenic applications. This material will be ideally suited for applications where vacuum jacketed insulation proves uneconomical, and where the current foams and foam-glass fail prematurely due to thermal cracking of the vapour barrier, leading to moisture attack [Unique, Sprayable, Syntactic Foam Insulation for Cryogenic Application].

A design concept for composite wind tunnel compressor blades at NASA Ames Research Center was based on a sandwich construction composed of carbon fibre-reinforced polymer (CFRP) skins bonded to a syntactic foam core [Jize et al., 1996].

Syntactic foams have found use in ISRO’s mission too. To prevent heating due to aerodynamic friction, the heat shield of PSLV/GSLV are coated with silicone based syntactic foam (PMC-30). The same coating is used as thermal insulation in cryo liquid tanks. The phenolic based medium density ablative (MDA) and low density ablative (LDA) have been used to provide thermal protection to the base of the Satellite Recovery Experiment. Such systems have potential for use as TPS in future manned/unmanned mission.

The leading edge honeycomb panels of Airbus A330/340 have been built by The Aerostructures Corporation since 1989. The upper leading edge panels are fabricated of woven fibre glass skins and Nomex honeycomb, whereas the lower edge panels are fabricated of woven carbon skins and Nomex honeycomb. In addition, around the panel periphery, the lower carbon skins use Syncore syntactic foam between carbon plies [Nelson, 1997]. Some aircraft designs now use syntactic foams in place of honeycombs,
especially in parts of the structure that are highly contoured or involved with communication, navigation, or radar antennas. While honeycombs are suited for simple flat panels, for aircraft applications, with their many antenna installations and highly contoured moldlines, there's no substitute for syntactic foams.

1.4.9.4 In radomes

Honeycomb structures which are used in sandwich panels of radomes are highly orthotropic. i.e. the properties will vary with direction, which leads to unpredictable signal propagation in radomes. Also, the strength and stiffness of honeycomb sandwich panels will vary with direction of loading. Other properties, like dielectric constant and thermal conductivity are also affected. All these problems can be solved by the use of syntactic foam core sandwich composites [Cattanach, 1989]. Radomes can be made entirely from syntactic foam with an outer protective rain-erosion covering. The density, and hence the dielectric constant of syntactic foams can be adjusted and specified to suit the particular radome applications.

1.4.9.5 In sports industry

New applications are coming up in sports industry, based on syntactic foams; snow skis and Adidas soccer balls are some of the examples. Bayer and Adidas produced high tech soccer balls for EUFA EURO 2004 Championship. The new official ball, called the “Fevernova” is highly resistant to abrasion and has very low water absorption property. The surface material of the ball is a high-solid polyurethane coating. Beneath the surface is an elastic layer of Impranil, a syntactic polyurethane foam with low-temperature flexibility. The foam consists of equal sized, highly elastic, exceptionally resistant gas-filled microcells. This composite ensures an especially good ball feel and good damping properties. According to Adidas, the ball returns energy
equally at all points on the ball, which makes the flight of the ball more accurate and more predictable than any previous ball. Moreover, the foam is highly elastic, so more of the force is transferred to the ball when it is kicked, causing it to travel faster [Fuming over the World Cup’s Foam Ball; Players Bawl over Ball; Bayer and Adidas].

1.4.9.6 Furniture applications

The materials used in the construction of modern articles are undergoing a radical change. Therefore, attention has been focused by material scientists to develop polymer based materials to substitute wood for a variety of applications. The use of cast thermoset resins to make furniture parts is growing rapidly despite the problems of high density and brittleness. Syntactic foams are examined as ways to solve these problems without loss of the inherent advantages of cast thermosets namely short initiation time from master to production parts, low equipment costs, low mould cost, high quality detail reproduction, easy finishing, low part cost, and fast cycle times [Mukherjee and Saraf, 1994].

Among the organic polymeric microspheres, saran microballoons give the best results for the fabrication of synthetic wood. Saran microspheres are generally expandable thermoplastic spheres composed of polyvinylidene chloride (PVDC) coreacted with other monomers to form a micron sized shell, encapsulating a low boiling hydrocarbon. In polyester synthetic wood castings, saran microspheres offer many advantages over other commonly used lightweight fillers [Mukherjee and Saraf, 1994].

1.4.9.7 As synthetic marble

The major drawbacks of natural and synthetic marble are their weight and low impact strength. The use of microspheres in synthetic marble formula can reduce the
weight of parts produced to one-half or less while eliminating the need for titanium dioxide pigment. The products containing microspheres have a translucency resembling natural marble. They have high resistance to impact breakage and low flexural and compressive strength. When a gel-coat is used, stain resistance is comparable to that of the heavier synthetic marble [Anderson et al., 1970].

1.4.9.8 Shape memory syntactic foams

Shape memory syntactic foam systems have been introduced by Cornerstone Research Group (CRG), Inc. under the trade name Verilyte. Verilyte can function as deployable or conformal composite foam core in its softened form, or as a structural foam core in its rigid state. Figure 1.13 illustrates the compressed and expanded form of shape memory syntactic foam. Current developmental formulations have densities ranging from 100-400 kg/m$^3$, with expansion ranging up to 400%. These qualities provide the ability to fabricate adaptive composite structures with foam core, soften the structural foam element, alter its shape, and then return to a rigid state in its new configuration. Verilyte can be reshaped several times. Its possible applications include dynamic structural support, flexible foam core, and expandable foam fill [Verilyte, CRG, Dayton, OH, USA].

1.4.9.9 Plug assist materials

Trelleborg Emerson & Cuming, Inc. makes syntactic foam plug assist materials, known as Syntac, using high purity, hollow glass microballoons in a high-performance epoxy matrix. These materials have outstanding consistency, low void-content and easy, low-dust, high-speed milling. The advantages of syntactic foam plug assists include even sheet distribution, elimination of webbing, dimensional stability at high temperature, lower thermal conductivity, easy handling, better durability than
wood etc. Syntac maintains its hardness right up to its specified maximum running temperature and exhibits excellent abrasion resistance. It is a lightweight, durable and cost effective alternative to wood, felt, aluminium and derlin. Syntac plug material is engineered to address problems inherent in traditional thermoforming tooling such as sticking, deformation and failure. Syntac plugs exhibit extremely low thermal conductivity, so they do not draw heat away from the sheet, virtually eliminating the primary cause of plug sticking or fouling. Syntac plugs are quick and easy to replace and are repairable if subjected to a minor damage. Aircraft manufacturers that include Airbus and Boeing, reinforce hollow areas within the aircraft with syntactic foam [Syntactic Foam adds Strength and Buoyancy].

Figure 1.13 Compressed and expanded forms of shape memory syntactic foam made by CRG [Verilyte, CRG, Dayton, OH, USA]

1.4.9.10 In graphitic printing

Syntactic foams are suitable for printing two and three-dimensional graphic designs and the like on various substrates including paper and textile fabrics. Syntactic foam graphic arts print media are particularly suitable for application to a substrate using high speed mechanical printing processes. The application involves adding to a
basic print medium a minor amount of pre-expanded, nonfriable, polyvinylidene chloride based microspheres substantially heat stable between about -20° C and 175° C, having a particle size of about 10 to 100 µm in diameter, to produce syntactic foams having unlimited shelf life. The print media thereby produced may be applied to any known substrate in any desired graphic pattern [Melber, 1990].

1.4.9.11 In underwater sound transducers

Underwater sound transducers are often employed under high hydro-pressure. To realise a transducer with the desired directivity in the deep sea, a new transducer construction has been devised in which a syntactic foam is attached to a sensitive cylindrical element. Syntech Materials, Inc. combines syntactic foam technology with advanced acoustics theory to develop a novel class of underwater sound attenuators. These materials, known as the SADM (Syntactic Acoustic Damping Material) and the SATB (Syntactic Acoustic Transducer Baffle) families of syntactic foams, have repeatedly shown high levels of echo reduction and insertion loss over the 10 kHz -100 kHz range, both at ambient pressure and at operating depth. Two types of materials are available: the -1 series for broadband attenuation and -0.5 series for improved performance at higher frequencies (above 30 kHz). These materials have been found to be extremely effective in a number of underwater acoustic applications. SADM has been used extensively as an anechoic acoustic test tank lining. SATB is used as a transducer isolation mounting material [http://www.syntechmaterials.com].

1.4.9.12 Miscellaneous applications

In the production of disposable drinking cups and plastic packaging, syntactic foam is used because it is a highly durable material capable of withstanding the millions
Chapter 1

of cycles associated with repetitive thermoforming [Syntactic Foam adds Strength and Buoyancy].

TG Grade syntactic foams manufactured by Trelleborg Emerson & Cuming, Inc. have been used in mine neutralisation systems because of their zero magnetic and seawater comparable acoustic signatures.

If a military vehicle drives over a device such as a landmine or IED (improvised explosive device) the outer metal structure often protects the occupants from injuries caused by shrapnel penetration. However, shock waves from the explosion can often result in serious injuries. Syntactic foams act as a shock absorber to reduce this risk of serious injury. They provide a field installable protection against explosive devices for floorboard undercarriage shield, door guards and firewalls. Damage is minimised as are the effects of fire and secondary explosions [Syntactic foam blast protection system].

Improved syntactic foam replaces graphite composite in Jet Engine Nacelle. The syntactic foam loaded with high compressive strength microspheres is sandwiched between thin layers of composite. The foam core combines a 350 F cure epoxy with the glass microspheres and has a thin non-woven Kevlar carrier. The material was developed by American Cyanamid [Advanced Materials Newsletters].

Elastomeric syntactic foams have been developed for use as stress relief coating on electronic components in encapsulated assemblies. These foams have been made with various castable thermosetting elastomers and microbubbles [Kenig et al., 1984; Rand, 1978].

Syntactic foams are also employed in electronics and telecommunications due to superior thermal and dielectric properties [El-Hadek and Tippur, 2003]. They are also
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employed in electronics and telecommunication fields for shielding electronic components or cables from vibrations, electromagnetic fields, radiations and high temperatures [Rizzi et al., 2000].

Due to the high specific energy absorption, and impact resistance, syntactic foams have been considered for army vehicles and for personnel protection [El-Hadek and Tippur, 2003]. Microwave transparency of syntactic foam gives an additional advantage in military aviation [Gupta, 1999]. In motorcar industry, syntactic foams have been used for spoilers, dashboards and roofs [Rizzi et al., 2000].

Carbon-carbon syntactic foams find application as furnace electrodes, insulant for high temperature furnaces and as filter material for corrosive chemicals and gases. Syntactic foams based on saran microspheres are used as fibre glass reinforced backup for vacuum formed acrylic structures and in sandwich panel constructions.

Carbon microspheres combined with carbonaceous matrix, polyimide or epoxy resins are used as high temperature insulation materials and in some cases, due to their appropriate electronic conductivity, they may be used for attenuating electromagnetic energy [Calahorra et al., 1987].

Thus, all the areas of science and technology have benefited from the advancement in technology of syntactic foam materials with special features and this has given a lot of scope for research in this area.
1.5 Scope and objective of the present work

The literature survey on syntactic foams, as compiled in chapter 1, reveals that it is an active area of research. A large volume of research has already been carried out in the area of syntactic foams based on diverse polymer systems that has resulted in the emergence of a variety of products for specific applications. The properties of syntactic foams are dictated by nature of resin, microballoon, reinforcement, their proportion and the way they are dispersed in the matrix. The resin has a decisive role in dictating the composite properties, especially its thermal and thermo-physical characteristics. Among the thermoset resins, the most versatile one is epoxy resin that has been quite exhaustively explored in the design of diverse syntactic foams. Epoxy systems are limited by low toughness, low $T_g$ and low temperature serviceability. For structural and particularly thermo-structural applications, phenolics are the matrices of choice. Phenolic resins have obvious advantages in view of their enhanced thermal stability, high $T_g$, char yielding property that render them the resin of choice for thermo-structural applications particularly in aerospace industry. Thus, phenolic based syntactic foams still draw the attention of aerospace researchers. However, the inherent brittleness of phenolic resin is an everlasting issue. To address this, cyanate ester has emerged as a compromise matrix system encompassing the thermal stability of phenolics and processability of epoxies. Cyanate ester is poised to replace epoxies in structural applications and phenolic-cyanate ester is an improved version of phenolics for thermo-structural applications. It can be seen that cyanate ester evinces a lot more interest of researchers. However, cyanate ester based syntactic foams have hardly been reported. The objective of the thesis is to explore the area of syntactic foams based on cyanate ester for possible structural applications and phenolic syntactic foams for thermo-structural applications.
Cellular foams based on cyanate ester using azodicarbonamide as foaming agent were attempted. However, processing of cyanate ester foams through this route suffered from the disadvantage of high exothermicity of the curing reaction. Thus, the main objective of the present study has been on exploring the syntactic foams of cyanate ester, in which the difficulties associated with the processing of conventional polymer foams could be obviated. The effect of microballoon nature and its volume percentage on the properties of cyanate ester syntactic foams has been studied. Subsequently, cyanate ester syntactic foams were evaluated as core in sandwich composites. Studies were carried out to improve the properties of the syntactic foams by incorporation of glass fibre and nanoclay.

The latter part of the study deals with phenolic syntactic foams which have potential application as thermo-structural systems in space applications. The effect of microballoon concentration on the properties of phenolic syntactic foams has been studied. The syntactic foams based on conventional phenolic resin and an addition curable phenolic resin (propargyl ether novolac) were explored. The mechanical, dynamic mechanical, thermo-physical and ablative properties of silica fibre reinforced phenolic syntactic foams have been investigated in detail. The system was examined as thermal protection system under simulated atmospheric re-entry conditions.

The work carried out in the above direction has been described in the thesis, divided into 10 chapters. Chapter 1 (present chapter) gives a summary of the literature survey carried out on syntactic foams. The basics of syntactic foams, general methods of preparation and properties of syntactic foams, types of syntactic foams, recent advances in this field and applications of syntactic foams are covered in this chapter. Different polymer systems have also been discussed.

Chapter 2 gives a brief description of the materials used and the test methods adopted for the evaluation of the polymer and foam/foam composites.
Chapter 3 describes processing of cellular foams based on cyanate ester and the
effect of foaming agent concentration on the processability and the compressive
properties of the foams.

Chapter 4 is devoted to the studies on syntactic foams based on bisphenol A
based cyanate ester. The effect of nature and volume fraction of glass microballoons on
the mechanical and dynamic mechanical properties of the foams is presented.

In chapter 5, cyanate ester syntactic foams have been evaluated as core in
sandwich composites. The effect of core composition on the mechanical properties of
the sandwich composites has been investigated.

Glass fibre- and nanoclay-reinforced cyanate ester syntactic foams constitute the
subject of chapter 6 and 7 respectively. The effect of glass fibre and nanoclay on the
properties of the cyanate ester syntactic foams has been studied.

Phenolic resins were also explored as matrix resin in foam composites. The
studies on processing and the mechanical and dynamic mechanical properties of
phenolic syntactic foams are described in chapter 8. The properties of the foams based
on conventional phenolic resin and propargyl ether novolac resin are compared in this
chapter.

Silica fibre reinforced phenolic syntactic foams were evaluated as low density
ablative thermal protection systems under specified atmospheric re-entry conditions.
The details of the mechanical, thermal, thermo-physical properties and thermo-
responsive simulation studies are compiled in chapter 9.

The important conclusions from the present studies and the scope for future
work in the area are summarised in the final chapter.