PROPERTIES OF CEMENT SYNTACTIC FOAM COMPOSITE FOR SOUND INSULATION APPLICATION

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PROPERTIES OF CEMENT SYNTACTIC FOAM COMPOSITE FOR SOUND INSULATION APPLICATION

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CB	Carbon black
CHS	Cement hollow spheres
CFD	Computational Fluid Dynamic
CSF	Cement syntactic foam
CT	Computed tomography
EPS	Expandable Polystyrene
FDM	Finite difference method
FEM	Finite element method
FSI	Fluid Structure Interaction
FVM	Finite volume method
GPU	Graphic Processing Unit
HS	Hollow spheres
MMSFs	Metal matrix syntactic foams
MRTLBM	Multiple-relaxation-time lattice Boltzmann method
OPC	Ordinary Portland Cement
PANI	Polyaniline
PC	Plain cement
PDADMAC	Poly(diallyldimethylammonium chloride)
SEM	Scanning Electron Microscopy
SF	Syntactic foams
SiO_2	Silicon Dioxide

TiO_2	Titanium Dioxide
TL	Transmission loss
UDF	User Defined Function
GFR-HEMS	Glass fiber reinforced hollow epoxy macrosphere
FC	Foam concrete
LAC	Lightweight aggregate concrete
LAFC	Lightweight aggregate foamed concrete
GFC	Geopolymer foam concrete
EDS	Energy dispersive x-ray spectroscopy
AE	Air entrained

LIST OF SYMBOLS

%	Percentage
<	Less than
>	More than
mm	Millimetre
°C	Degree Celsius
P_M	Pressure Amplitude
P_{RMS}	Root-Mean-Square Amplitude
Pa	Pascal
λ	Wavelength
f	Frequency
Hz	Hertz
T	Period
α	Sound Absorption Coefficient
τ	Sound Transmission Coefficient
dB	Decible
v_v	Void Volume
ε	Porosity
v_o	Entire Body Volume
ρ_f	Density of Foam Material
ρ_o	Density of Solid Material
u	Fluid Velocity
ΔP	Pressure Drop
L	Length of Porous Medium

ρ	Fluid Density
d_p	Average Diameter
β	Inertial Resistance
$1/\alpha,$	Viscous Resistance
kg/m^3	Kilograms per Meter Cubic
η	Radius Ratio
r_i	Inner Radii
r_o	Outer Radii
ρ_a	Apparent Density
m_{chs}	Weight of CHS
v_{chs}	Volume of CHS
ρ_t	True Density
m_{wall}	Weight of CHS Wall
v_{wall}	Volume of CHS Wall
v_f	Volume Fraction
ρ_{exp}	Experimental Density
m	Mass of Sample
v	Volume Sample
ρ_{CSF}	Density of CSF
ρ_{PC}	Density of PC
V_v, chs	Hollow Fraction of the CHS Volume
V_v	Matrix Porosity
ρ_{CHS}	Density of CHS
ρ_{CM}	Density of Cement Matrix
V_T	Total Porosity
mm/min	Milimeter per minute

d	Diameter
c	Speed of Sound in Air
l	Length of Tube
Hz	Hertz
I	Intensity
W	Power
S	Area Passed Through by Sound
p	Sound Pressure
ρ_0	Air Density
ξ	Displacement
z	Characteristic Impedance of Media
s	Second
g/cm^3	Gram per Centimetre Cubic
σ_{CHS}	Compressive Strength of CHS
MPa	Megapascal

SIFAT-SIFAT KOMPOSIT BUSA SIMEN SINTAKTIK BAGI KEGUNAAN PENEBATAN BUNYI

ABSTRAK

Suatu teknik inovatif untuk menghasilkan komposit busa simen sintaktik (CSF) telah dicadangkan dalam projek penyelidikan ini. Bahan selular komposit ini pada dasarnya terdiri daripada matriks simen yang dibenamkan dengan sfera berongga simen (CHS). Pendekatan yang mudah dan inovatif dilaksanakan dalam penyediaan CHS di mana manik polistirena terkembang (EPS) digunakan sebagai bahan pemula untuk menjana sfera berongga. Manik EPS telah disalut dengan resin epoksi dan serbuk simen, kemudiannya dimatangkan dan dipasca matang. Proses ini mengecutkan EPS manik seterusnya menghasilkan struktur sfera berongga. CHS disalut dengan satu, dua dan tiga salutan untuk membezakan ketebalan dinding. Komposit CSF yang dihasilkan daripada CHS dengan satu, dua dan tiga salutan dirujuk sebagai CSF-1x, CSF-2x dan CSF-3x. Proses penentuan awal jumlah CHS sebelum fabrikasi CSF komposit telah memberikan susunan sfera yang optimum untuk mencapai taburan rongga yang sekata. Kaedah ini telah berjaya mengurangkan ketumpatan CSF-1x, CSF-2x and CSF-3x, kepada 51%, 47% dan 41% berbanding simen biasa (PC). Kekuatan mampatan untuk CSF-1x, CSF-2x and CSF-3x masing-masing adalah 8.9, 11.7 dan 13.3 MPa. Adalah didapati bahawa CSF yang digabungkan dengan CHS yang bersalutan lebih tebal menunjukkan kekuatan mampatan yang lebih tinggi berbanding dengan yang digabungkan dengan CHS yang bersalutan nipis. Corak-corak kegagalan di dalam sampel ujian juga telah diperiksa untuk menentukan mekanisma kegagalan itu. Pemerhatian ini menunjukkan bahawa

kedua-dua CSF mempamerkan kegagalan jenis ricih tetapi mempamerkan berbagai jenis patah retak kerana perbezaan pada ketebalan dinding CHS. Ujian akustik (penyerapan bunyi dan kehilangan penghantaran bunyi) telah dijalankan untuk mengkaji tingkah laku akustik CSF berbanding dengan simen biasa (PC). Pekali penyerapan bunyi dalam busa simen sintaktik pada frekuensi 400 Hz hingga 1600 Hz adalah dalam julat 0.15 hingga 0.25, di mana simen biasa adalah di bawah 0.15. Peningkatan ketara penyerapan bunyi dalam CSF berbanding dengan PC adalah disebabkan boleh kehadiran keliangan terbuka yang digabungkan dengan liang dalaman yang kasar di permukaannya. Struktur yang kasar dan berliang itu membolehkan pelesapan gelombang bunyi yang agak besar melalui geseran apabila ia bersentuhan dengan permukaan sampel CSF, maka membawa kepada pekali penyerapan bunyi yang tinggi. Kehilangan penghantaran bunyi dalam busa simen sintaktik pada frekuensi 400 Hz hingga 1600 Hz adalah dalam julat 20 dB hingga 60 dB, di mana simen biasa adalah dalam julat 60 dB hingga 80 dB. Struktur sel tertutup dalam CSF menghalang laluan udara, lalu memberikan rintangan yang tinggi untuk perjalanan gelombang bunyi yang sama seperti dialami oleh PC. Kajian simulasi telah berjaya dilakukan dengan menggunakan pakej perisian ANSYS-FLUENT 14. Simulasi tersebut berjaya menggambarkan interaksi antara sifat-sifat bahan dan tekanan bunyi yang sukar dicapai dalam suasana makmal.

PROPERTIES OF CEMENT SYNTACTIC FOAM COMPOSITE FOR SOUND INSULATION APPLICATION

ABSTRACT

An innovative technique, in producing Cement Syntactic Foam (CSF) composite, is proposed in this research project. This cellular composite material consists of a cement matrix embedded with in-house developed Cement Hollow macrosphere (CHS). Simple and innovative approach was implemented in the preparation of CHS where expanded polystyrene (EPS) beads were used as initiation material to generate the hollow sphere. The EPS beads were coated with the epoxy resin and cement powder, were later cured and post-cured at high temperature. This process shrinks the EPS beads thus producing a hollow sphere structure. The CHSs were coated for second and triple coating as to vary the wall thicknesses. The CSF composites produced by CHS with single, double and triple coatings are referred as CSF-1x, CSF-2x and CSF-3x, respectively. The process of pre-determined amount of CHS before fabricating the CSF composite, gave an optimal packing of sphere as to achieve well distributed void. This step successfully reduced the density of CSF-1x, CSF-2x and CSF-3x, almost 51%, 47% and 41% respectively in comparison to the control plain cement (PC). The compressive strengths of CSF-1x, CSF-2x and CSF-3x were 8.9, 11.7 and 13.3 MPa, respectively. From the comparative compressive properties of CSFs it were found that the CSF incorporated with thicker-coatings of CHS showed a higher compressive strength than that incorporated with thinner-coatings of CHS. The failure patterns within the test samples are examined to

determine the failure mechanism. These observations show that both CSFs exhibited shearing type failures, but with different types of crack fractures caused by differences in CHS wall thicknesses. Acoustic tests (sound absorption and sound transmission loss) were conducted to examine the acoustic behaviour of CSF in comparison to PC. The sound absorption coefficient in CSF at frequencies of 400 Hz to 1600 Hz was in the range of 0.15 to 0.25, whereas the PC was below 0.15. The significant improvement of sound absorption in CSF over PC can be attributed to the presence of open porosity combined with rough internal pores on its surface. This rough and porous structure allows considerable sound wave dissipation via friction when in contact with the CSF surface sample; thus raising the sound absorption coefficient. The sound transmission loss in CSF at frequencies of 400 Hz to 1600 Hz was in the range 20 to 60 dB; whereas the PC was in the range 60 to 80 dB. The closed-cell structure of the CSF prevented the passage of air, thus giving high resistance to the sound wave's travel as similarly experience by PC. The simulation study was successfully performed using ANSYS-FLUENT 14 software. From the simulation, it was found that the interaction between the properties of the material and sound pressure can be visualized; which usually is difficult to achieve in a laboratory setting.

CHAPTER ONE

INTRODUCTION

1.1 Preamble

Noise, which is described as sounds that are unpleasant and disturbing, has become a major irritant that is negatively influencing the lives of many people on a daily basis (Caciari *et al*., 2013; Goines and Hagler, 2007). Noise emanates from human activities, particularly as a result of the growth of cities, advancements in the field of transportation, and industrial development (Singh and Davar, 2004; Goines and Hagler, 2007). According to the Guidelines for Community Noise issued by the World Health Organization, sounds, if left unchecked, can lead to noise pollution, which in turn may have an impact on the physical and mental wellbeing of the people. Thus, studies have been carried out to discover various methods for curbing undesirable sounds, such as the use of isolators or damping panels to reduce noise and vibrations, the use of barriers to block the entry of noise into a specific area, and the application of certain materials to absorb sounds in order to disperse excessive sound energy.

One way to deal with this issue is to develop sound isolation materials. These can be categorised, among several others, as insulation materials, sound absorption materials, vibration isolation materials, and damping materials, of which insulation materials are the most important and are being used extensively in various industries, including the construction, electronics and automobile industries. The majority of the studies into this area have concentrated on the use of common materials like gypsum, plywood, asbestos and concrete, to construct insulation materials made up of one or more layers of board on either side (Guillen *et al*., 2008; Warnock, 1998). The insertion of sound absorbing materials, such as glass wool and rock wool, into the partition cavity was also considered in order to enhance the sound insulation (Bravo *et al*., 2002). However, these materials can have serious consequences on the health of the lungs, eyes, and skin, and cause many other problems. Of late, researchers have been focusing their attention on integrating the use of smart materials into insulation materials instead of designing structures to obstruct the sounds.

1.2 Foam composite

Foam composite has been attracting a lot of attention for the use of an insulation material that can both impede and absorb sound, because of its distinct characteristics. Foam is a substance made up of pockets of gas cells distributed throughout a solid or liquid. Foams can be either closed- or open-cell foams. The former consist of several discrete solitary cells, while the latter consist of cells that are linked to one another, thus permitting the flow of a liquid through them. Foam material is used for sound insulation due to the structure of its cells. The open-cell foam material, which allows sound to flow through, is ideal for sound absorption, while the closed-cell foam material, which blocks the flow of sound, is suitable for sound proofing. In addition, the cell structure also helps to reduce the density, thus making the foam material lightweight. These two criteria, namely insulation capabilities and lightweight, are sought in materials for the design of various applications such as automotive parts, aerospace components, sound-proof rooms (e.g. recording studios, meeting rooms and theatres), and even for the purposes of safety at the workplace.

Polymeric foams are used extensively in these applications as they have superior insulating properties for both thermal and acoustic insulation, as well as shock and impact absorbing properties. Nevertheless, polymeric foams have a weak structure as they are not very stiff, are poor conductors of heat and are not fire-resistant. As such, metal foams, which are light, very stiff and high in strength, are ideal for applications that require materials that can sustain loads and absorb impact energy. However, metal foams corrode easily when exposed to the environment. The search for a solution to these problems led to the discovery of cellular cement, a lightweight material that is strong, has a high level of stiffness and is also cheaper than other foam materials (Huang and Liu, 2001; Ramamurthy *et al.,* 2009; Just and Midendorf, 2009).

Syntactic foams, which are a distinctive class of closed-cell foams introduced in the 60's, are produced by inserting hollow spheres or microspheres, instead of introducing a foaming agent or pressurized compressed air, into a matrix material to form a cellular structure. Syntactic foam is classified under physical foams because instead of the matrix being foamed chemically, mechanical means are employed to fill the matrix with gas-containing particles. Thus, syntactic foam is completely closed-cell foam, which, unlike open-cell foams, has the advantage of low moisture absorption and high compressive strength. In addition, syntactic foam also has high energy absorption during deformation and high tolerance against damage. Syntactic foam also offers design flexibility since any material, such as a polymer, metal or ceramic, can be used to make the hollow sphere and matrix, depending on what properties are being sought in the composites.

1.2.1 Foam Concrete

Foam concrete (FC) is defined as a light cellular concrete (density of 400 kg/m^3 – 1850 kg/m^3) with random air-voids created from the mixture of foam agents in mortar (Amran *et al*., 2015). FC can be produced by either a chemical or mechanical foaming process. In the chemical foaming process, aluminium powder is normally added to cement slurry, whereby hydrogen bubbles will be produced by the reaction, and these are rapidly replaced by air in order to prevent it from being a fire hazard. On the other hand, in the mechanical foaming process, foaming agents are immediately added to cement slurry or these are pressurized by compressed air to obtain preformed foam, which is then shaken vigorously to form a stable mass. However, prior to designing the foaming process, many factors have to be taken into consideration such as the choice of foaming agents, the proportion of the mixture, the flow rate and the curing time for the foam (Ramamurthy *et al*., 2009) as these will contribute ultimately to the properties of the resultant FC, such as its density, strength and cell voids.

Lightweight aggregate foamed concrete (LAFC), is manufactured by incorporating various fillers, used as lightweight aggregate in cementitious composites as to attain reduced unit weight with better mechanical and functional properties. By introducing entrained air into LAFC, the density, acoustic and thermal properties of the concrete can be improved (Kim *et al*., 2012). Various fillers are used as lightweight aggregate in cementitious composite such pumice (Uysal *et al*., 2006), expanded perlite (Kramar *et al*., 2010), expanded polystyrene beads (EPS) (Tonyan and Gibson, 1992; Chen and Liu, 2013) palm kernel shell (Alengaram *et. al.,* 2013) and other materials. FC has been widely used as lightweight non and semi structural material for application to structural, partition, insulation and filling grades. The superior property such as low density helps to reduce structural dead loads, labour transportation and operating cost. The FC also provides the functional properties like fire resistance, thermal conductivity and acoustical properties as reported in a literature (Narayanan and Ramamurthy, 2000).

1.3 Problem Statement

Foam concrete (FC) has some potentially attractive properties for use as sound insulation material. It was reported that the sound insulation of FC can be influenced by the inclusion of foam content, amount, size and distribution of pores and its uniformity by using conventional foaming method (Amran et al., 2015). The studies on the acoustic cement/concrete foam material in the literature are being carried out with the aim of tailoring the pore structure by using this method, but not many of these studies are focusing on the use of syntactic foam, to improve the insulation against sound. Therefore, this study made use of syntactic foam to ascertain the acoustic features through the utilization of in-house developed cement hollow sphere (CHS) in a cement matrix to obtain cement syntactic foam (CSF) composites. This method resulted in the development of completely closed-cell cement foam with controlled cell size.

Several studies that have been conducted in relation to this type of foam have mainly used macrosphere made of glass, polymer, ceramic, carbon or metal, manufactured by reputable industries and utilize specialized equipment during processing (Korner and Singer, 2000; Gupta *et al*., 2014). In this study, CSF with low density, were prepared using an innovative processing approach that utilize a simple coating method for the production of CHS. The implementation of this innovative approach does not require any specialized equipment, thus lowering the production cost. In addition, the CHS were produced using similar material with the cement matrix, which is cement powder, thus minimizing the incompatibility at the interfacial region. It was reported that, the chemical reaction between the macrosphere and the matrix materials has detrimental effect on the load transfer and through that on the mechanical properties of the foam (Orbulov and Majlinger, 2010).

Most of the researches that have been published also examined the effects of varying the volume fraction and wall thickness of the macrosphere on the physical and mechanical characteristics of the foam (Gupta and Ricci, 2006; Porfiri and Gupta, 2009; Woldesenbet and Peter, 2009). It was noted that when the volume of the microspheres was increased, the density and strength of the syntactic foams were reduced. However, in this study, the properties of CSF are investigated by changing CHSs' wall thickness while keeping constant of its' volume fraction. This was followed by an evaluation of the failure mechanism and performance of the resultant CSF under compressive deformation with various wall thicknesses of CHS.

A study on acoustic properties of FC usually involves determination of sound absorption and sound transmission loss capabilities. The standard test methods normally used reverberation room, where the specimen under test is placed between the two room. The sound is generated in one room and measurement is taken in both the source and receiver room to characterize sound acoustic properties (Olynyk and Northwood, 2005). These methods are well defined, time tested and reliable, however implementing these testing methods requires a large piece of test material of 10 m^2 and a large room of about 100 m^3. In some cases, it is challenging to prepare a large and uniform specimen, thus a testing methods that is less costly and requires small specimen size would be of great interest in this situation. Thus, this study was carried out to determine sound absorption and sound transmission loss of CSF using an impedance tube, since it is faster and generally reproducible and requires relatively small circular sample, 100 mm in diameter.

The acoustic behaviour of systems consisting of perforated plates, porous materials and air cavities has been predicted in many studies by means of acoustic analyses (Howard, 2000; Ming-Hui *et al*., 2010; Parlar *et al*., 2013). Most of these studies involve the development of models to validate the analytical models by comparing them to the measurements obtained through the experiments, thus, frequently making the analyses very complicated and dependent on several factors such as the information on the geometries (size of the equipment, dimensions, thickness, placement of the sound source), the mechanical properties and the acoustic parameters. Although numerical-based models are very helpful and valuable tools, they have the disadvantages of being time-consuming and computationally costly. In order to minimize the factors and time consuming, a Computational Fluid Dynamic (CFD) model of the impedance tube with varying sample thickness was developed in this study by using the only parameter of porous properties of the sample. The interaction between the properties of the sample and sound pressure was monitored visually from the simulation, which is difficult to be achieved in an experimental setting.

1.4 Research Objectives

The primary objective of this research was to develop a CSF composites and determine its properties. The measurable objectives were:-

- To develop a completely closed-cell CSF composites using an innovative production approach by embedding in-house developed CHS with relatively controlled-sized cells and to examine the subsequent compressive properties of CSF in relation to the wall thickness of the CHS.
- To experimentally determine the acoustic behaviour (sound absorption and sound transmission loss) of CSF having different thicknesses.
- To simulate the pressure flow fields in the impedance tube by varying the thickness of Plain Cement (PC) and CSF composites samples by means of Computational Fluid Dynamics (CFD).

1.5 Scope of work

The scope of this work encompassed the experimental development of CSF composites, and the determination of its compressive properties and acoustic behaviour. The following stages were involved in the experimental and numerical investigations:-

- The production of CHS and the fabrication of a CSF composites.
- The determination of the CSF morphology, the average diameter of the CHS, as well as the wall thickness, density and porosity.
- Conducting mechanical compression test and acoustic tests (sound absorption and sound transmission loss).
- Construction of a three-dimensional (3-D) model of the impedance tube through the use of a GAMBIT 2.3.16 CAD processor.
- Simulation of the impedance tube by means of a ANSYS-FLUENT 14 solver under varying operational conditions in terms of thickness and porosity.

- Examination of the pressure flow profiles obtained from the simulation study in relation to the acoustic behaviour obtained experimentally.

1.6 Thesis Outline

This thesis was organized into five chapters. Chapter 1 dealt with introduction, including problem statement, objectives and scope of work. In Chapter 2, the literature review covers the topic of syntactic foam, acoustic and simulation study. The methodology was presented in Chapters 3, where it comprised two segments. First segment described the experimental study including raw material selection, processing, characterisations and testings. Second segment described numerical setup such as computational model and simulation study. Results, discussion and comparison study were presented in Chapter 4. Finally, conclusion and recommendation for future works was discussed in Chapter 5.

CHAPTER TWO

LITERATURE REVIEW

2.1 Syntactic foam

Syntactic foam—the concept of introducing a lightweight material in a matrix—was introduced in the 1960s. The term syntactic is derived from the Greek word *syntaktikos* which means 'to arrange together' (John and Nair, 2010). This material is classified as a foam since it possesses cellular structure in nature. As defined by the American Society for Testing and Materials (ASTM), syntactic foam is a "material consisting of hollow sphere fillers in a resin matrix". Thus, it is also known as particulate foam composite since the hollow spheres can act as reinforcement in a matrix.

Syntactic foam consists of preformed hollow glass, ceramic or polymer spheres dispersed within a matrix or binder, which has several applications. This foam can be distinguished from traditional foam by the method it is produced. For instance, compared with traditional foam—produced by foaming the matrix material chemically or through gasification—syntactic foam is produced by dispersing the hollow spheres mechanically into the matrix, and thus it is also known as physical foam.

In general, syntactic foam can be tailored for optimum performance. The desired properties can be constructed and predicted by selecting suitable hollow spheres and binder combination, giving this foam "tailorability" which is not possible with conventional foaming operation—which tends to create more random cellular arrangements. In addition, dispersing the hollow spheres in a matrix makes this type of foam absolutely a “closed cell” foam, giving it a higher strength advantage as well as minimal moisture absorption coefficient compared to the “open-cell” foam. The spherical geometry of the hollow sphere—normally used as filler in a matrix—allows the best packing factor and hydrostatic compression strength.

Syntactic foam is extensively used in civil and industrial engineering as imitation wood and for other building construction purposes for its shear stiffness and higher specific strength. Naval and marine equipment manufacturers find it ideal for decks and submarines buoys as well. Likewise, due to its high specific energy absorption and impact resistance, syntactic foam is used as core material of sandwich structures. It is also employed in electronics and telecommunications projects due to its superior thermal and dielectric properties as well as shock absorption characteristics. Additionally, the ‘closed-cell’ structure of syntactic foam makes this type of foam potentially effective as a sound and thermal insulation material.

2.1.1 Processing of hollow spheres in syntactic foam

Hollow spheres play a key role in generating cellular structure, which gives the syntactic foam its low density, high specific strength, and low moisture absorption. Hollow spheres are characterised by their particle size, wall thickness, and density. Hollow spheres ranging from 1-50 μm diameters are known as microspheres (John and Nair, 2010). Other terms used in syntactic foam literature which refer to the hollow microspheres are microballoons and cenospheres. Cenospheres are the hollow particles in fly ash formed by the rapid cooling of glass during the combustion process of coal. For hollow spheres with a diameter up to 0.3 mm, the term used is hollow macrosphere (John & Nair, 2010).

Over the years, a variety of processing methods have been developed to produce hollow spheres, such as spray and coaxial-nozzle method, the sacrificial-core method, and the sol-gel/emulsion method. The summary of the advantages and disadvantages of each method was presented in Table 2.1.

Table 2.1: Summary of the advantages and disadvantages of the hollow sphere processing methods

Method	Advantage	Disadvantage	References
Spray and coaxial-nozzle method	• most suitable for bulk production and large diameter spheres. • capable of producing mono-sized hollow spheres with uniform wall thickness	• depends on a number of factor: evaporation rate, concentration of the solution and droplet size	Scheffler and Colombo, (2005)
Sacrificial-core method	• diameter of the hollow sphere produced is controlled by the diameter of the template • the wall thickness is controlled by the concentration of the solution	• the process has a few step with variable control conditions such as precursor and template removal condition and exposure time	Matsuda *et al*., (2016) Scheffler and Colombo, (2005) Benham *et al*., (2011) Ohmi *et al*., (2006)

Table 2.1: Continued

Method	Advantage	Disadvantage	References
Layer by layer deposition	• greater flexibility in controlling the shell wall thickness of hollow spheres	• precise optimization of the reaction conditions is required to obtain uniform coatings and to avoid the occurrence of aggregation of the coated particles prior to core removal • the excess of polyelectrolyte must be removed which is time consuming • repeated use of centrifugal forces can disrupt the integrity of the layer	Mu *et al*., (2013) Caruso *et al*., (2001) Scheffler and Colombo, (2005)

2.1.1 (a) Spray and coaxial-nozzle method

In the spray and coaxial-nozzle techniques, a hollow sphere is prepared through a host of droplet generation techniques using solutions or slurries of the target material as the starting material. The solution or slurry is either sprayed through a hot chamber or through a coaxial nozzle set up to generate spherical droplets. These techniques are most suitable for bulk production and large diameter spheres (Scheffler and Colombo, 2005).

Specifically, spray pyrolysis and spray drying are two processes of the spray technique. When a solution is used for generating hollow spheres, the water or other organic solvents inside the liquid droplets act as blowing agent. In the spray pyrolysis process, to develop hollow ceramic sphere—for example, the hollow spheres are generated by atomising the inorganic precursor in solution form—

requires evaporating the solvent and precipitating the inorganic salt on the surface. The remaining solvent is removed by drying, and the precipitated salt is pyrolysed at high temperature (>250ºC) to form the desired ceramic phase in the shell of hollow spheres. Then, the pyrolysed spheres are sintered at high temperature to achieve sufficient mechanical strength.

Meanwhile, in spray drying, water or organic-based slurries are sprayed in the form of droplets into a chamber containing hot air or other inert gases. The schematic of spray drying is shown in Figure 2.1. This technique is applied to produce hollow spheres of TiO_2, hydroxyapatite and SiO_2 (Scheffler and Colombo, 2005).

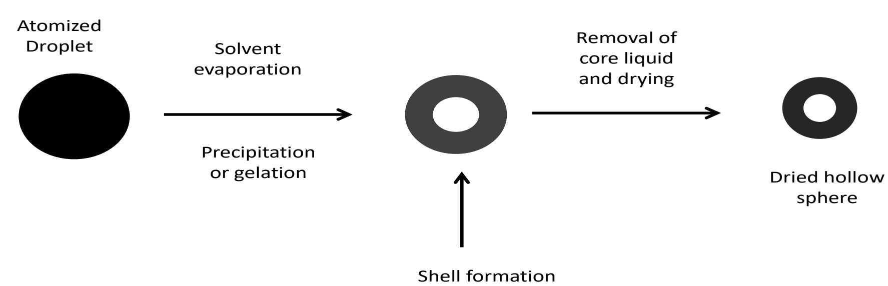

Figure 2.1: Schematic of spray drying (Scheffler and Colombo, 2005)

In a coaxial-nozzle method, a gas is blown through a nozzle concentric with an outer nozzle to generate spherical droplets containing gas. The size of the hollow sphere and the wall thickness are determined by the diameter of the outer nozzle, the spacing between the inner and the outer nozzles, and the slurry concentration. This process is capable of producing mono-sized hollow spheres with uniform wall thickness. Notably, hollow glass and ceramic spheres are among the hollow spheres produced through this process. The schematic of the generation of hollow sphere by the coaxial-nozzle technique is shown in Figure 2.2.

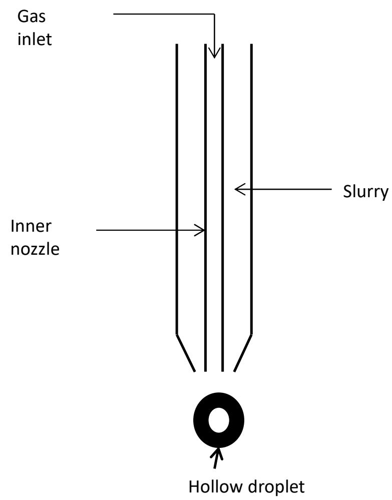

Figure 2.2: Schematic of hollow sphere droplet by using coaxial-nozzle technique (Scheffler and Colombo, 2005)

2.1.1 (b) Sacrificial-core method

The sacrificial-core method is one of the most widely used in producing ceramic hollow spheres (Cochran, 1998; Scheffler and Colombo, 2005). In this method, a spherical polymer particle—which functions as a core—is coated with a slurry or solution of ceramic material. The coated core is dried, and the core is removed by chemical dissolution or by heating to a temperature at which the polymer decomposes—leaving the core-shell. The thus-formed hollow sphere is heated to higher temperatures to sinter the particles in the wall and produce adequate mechanical strength and rigidity to the hollow sphere. In this method, the diameter of the hollow sphere produced is controlled by the diameter of the core or template particle, while wall thickness is controlled by the concentration of the solution used for coating the cores as well as the exposure time. Studies by Matsuda *et al*., (2016) found that the structure of the ceramic hollow spheres can be controlled with the retention of the spherical shape of the template by variation of the sintering temperature.

The sacrificial-core method is also applied in the production process of metallic hollow spheres (Benham *et al*., 2011; Ohmi *et al*., 2006). Prior to the coating process, the metal powder is suspended in a binder-solvent mixture. The suspension is then sprayed through a nozzle onto the rotating polystyrene beads. During the process, there is constant air flow, which enables the coated sphere to dry and sufficiently harden. The hardened coated sphere then undergoes a heat treatment to remove the polystyrene core through pyrolysis, and later, the hollow spheres are sintered at a high temperature of up to 1,000ºC.

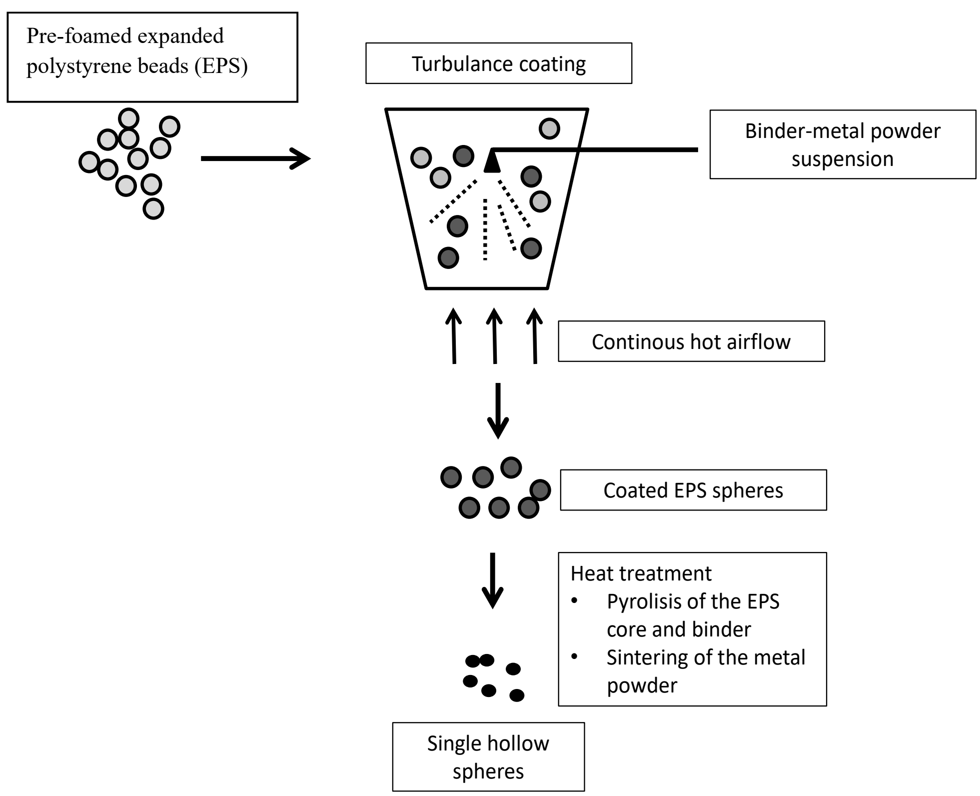

Figure 2.3: Schematic diagram of sacrificial-core method in producing hollow sphere (Scheffler and Colombo, 2005)

The rolling ball method classified as the sacrificial-core method was implemented in the preparation of glass fiber reinforced hollow epoxy macrospheres (GFR-HEMS) was reported by Wu *et al.*, (2015). In this method, GFR-HEMS was prepared by using a rolling ball machine and glass fiber was added into the epoxy hollow sphere to improve the compressive strength of the macrosphere. The EPS beads were used as intermediate material to develop GFR-HEMS. The EPS beads were coated with epoxy resin and glass fiber, and were later cured and post cured at high temperature to shrink the EPS beads thus producing a hollow macrosphere structure. This method has been producing GFR-HEMS having different wall thicknesses with the density of 240-650 kg/m^3. The wall thicknesses were examined under the scanning electron microscopy (SEM) and found to be in the range of 0.208-0.669 mm.

2.1.1 (c) Layer by layer deposition

Layer by layer deposition can be viewed as a variation of the sacrificial-core method, but it gives greater flexibility in controlling the shell wall thickness of hollow spheres. Basically, this method involves the alternating adsorption of charged species onto oppositely charged spherical core/template using inter-molecular interactions as the driving force, such as electrostatic interaction, hydrogen, and covalent bonding. To obtain the hollow spheres, the core/template is removed by thermal or chemical means. Various types of hollow spheres prepared by this technique have been reported in the previous literature (Mu *et al.*, 2013; Caruso *et al.*, 2001; Scheffler and Colombo, 2005).

For instance, Mu *et al*. (2013) prepared the polyaniline (PANI)/carbon black (CB) hybrid hollow microsphere by the alternate adsorption of PANI and CB onto the polystyrene sulfonate microsphere templates after etching the templates by dialysis. They found that with the properties of each material used these hybrid hollow microspheres would be potential candidates as electrode materials for supercapacitors with high specific capacitance.

In ceramic hollow spheres, adsorption of positively charged polyelectrolyte such as poly(diallyldimethylammonium chloride) (PDADMAC) onto the polystyrene (core material) in solution leads to a formation of the polyelectrolyte layer. A ceramic particle which is negatively charged is then adsorb onto the polyelectrolyte layer by electrostatic interaction. By repeating the process of alternating adsorption of polyelectrolyte and ceramic particle layers, the required wall thickness of the hollow spheres is obtained. The core is removed by thermal or chemical means, and the resulting green hollow spheres are generally sintered at temperatures of above 400ºC (Scheffler and Colombo, 2005).

The parameters governing generation of the hollow spheres depend on the selection of the core materials, polyelectrolyte, particle size, shape and concentration the solution, inorganic molecular precursor, core removal and sintering temperature of the hollow spheres (Caruso et *al*., 2001). In the case of ceramic hollow sphere, it is possible to control the wall thickness of the hollow sphere by the number of cycles used to deposit polyelectrolyte and ceramic layers, however the excess polyelectrolyte must be removed each time the ceramic layer is adsorbed or coated onto the polyelectrolyte, which is time consuming. In addition, repeated use of centrifugal forces for this purpose can disrupt the integrity of the ceramic layer (Scheffler and Colombo, 2005).

2.1.2 Fabricating of syntactic foam

Syntactic foam can be fabricated by mechanically incorporating prefabricated hollow spheres-type of carbon, glass, alumina, glass, and other materials in metallic or polymer matrices to make syntactic foam composite. Since the hollow spheres have lower density than the matrix, the resulting composite have lower density than that of the matrix as well. Various methods are found in existing literature, from simple blending of the components to novel coating methods on the hollow spheres surface (Kim and Plubarai, 2004; Scheffler and Colombo, 2005; Mondal *et al*., 2009; Rohatgi *et al*., 2011; Rivero, 2013). However, there are three methods of syntactic foam fabricating, which are widely discussed in related literature, namely pressure infiltration, stir casting, and blending/powder metallurgy and another method reported is the buoyancy method.

2.1.2 (a) Pressure infiltration

In pressure infiltration, appropriate amounts of hollow spheres are filled in a mould and the amount of matrix or binder is poured over it. A high pressure or vacuum—or a combination of both—is applied in the mould so as to allow the matrix or binder to penetrate into the interspheres voids. The advantages of this method include synthesis of syntactic foams containing high volume fraction of hollow spheres of up to 70 vol. %, net-shaped or near net-shaped component fabrication, and low porosity in the composite. On the other hand, the limitations of this method include the use of high pressure which causes hollow spheres to fracture, and low infiltration pressure which can lead to incomplete filling of pores and high residual porosity (Rohatgi *et al*., 2011).

Studies on syntactic metal-matrix foam—using pressure infiltration equipment—have been done by many researchers. For instance, Rohatgiet *et al*. (2011) fabricated metal-matrix syntactic using this technique on loose beds of hollow fly ash cenospheres with A356 alloy melt. They found that by using this technique, they can synthesise the composite in a wide range of cenosphere volume fraction, from 20% to 65%, and decrease the percent of voids.

2.1.2 (b) Stir casting

In the stir casting method, the preparation of the syntactic foam is by impregnation of hollow spheres into a matrix solution. The matrix solution is stirred using an impeller and the hollow spheres are slowly added. The mixture is then casted in a mould and allowed to cure. This method ensures uniform wetting of each hollow spheres by the matrix. In some cases, a coupling agent is added to surface treat the hollow spheres to enhance the interfacial bonding strength between the hollow spheres and the matrix (Scheffler and Colombo, 2005). The surface treatment also has the advantage of sealing the porosity in the hollow spheres. Subsequently, the stir casting's relatively low cost and easy implementation have resulted in its widespread use for fabricating syntactic foam. However, a volume fraction of the hollow spheres is a factor that should be given attention in this method. Flotation of the low density hollow spheres is a concern when a low volume fraction is used. On the contrary, at high particle volume fraction, high stir processing can lead to substantial hollow spheres fracture (Rohatgi *et al*., 2011). Studies on fabricating the syntactic foam using this method are cited elsewhere (Mondal *et al*., 2009; Rivero, 2013).

2.1.2 (c) Powder metallurgy

Powder metallurgy methods are widely used in fabricating metal-matrix syntactic foams. A wide variety of hollow spheres volume fraction can be incorporated in composite, thus making this method more versatile. In this method, matrix in powdery form are mixed together with hollow spheres in required volume fractions, and followed by compaction and sintering to obtain syntactic foams. However, the disadvantage of this method is the fracture of the hollow spheres during the compaction stage, especially at high volume fraction level. Thus, this method is more significant in fabricating syntactic foam containing low hollow spheres volume fraction (Vogiatzis *et. al*., 2015; Xue and Zhao, 2011).

2.1.2 (d) Buoyancy method

The other conventional method for fabricating syntactic foam as reported by the literature review involves the buoyancy method. Kim and Plubarai (2004) have investigated further the syntactic foam fabricating method involving the buoyancy of hollow glass spheres in epoxy resin. Their method involves shaking a mixture of hollow glass spheres and the epoxy resin in a sealed container before pouring the substance through a tube into a mould. A total time of three minutes was allowed to the hollow spheres for self-packing by the self-buoyancy in the mould. The hole at the bottom of the mould was then opened by removing a sealing tape, in order to drain the bottom layer of the liquid. Subsequently, the packed layer of the hollow spheres and liquid phase was slid down to the bottom of the mould and was left for 30 minutes. It was demoulded when the foam in the mould was sufficient.

2.2 Structure of the syntactic foam

The syntactic foam can be classified as a two-phase or a three-phase system. The two structures of the syntactic foam are schematically shown in Figure 2.4(a). The two-phase system contains only a close-packed arrangement of hollow spheres and a matrix; however, this is only a hypothetical situation. Essentially, it is difficult to avoid air entrapment in the system while mixing the constituents, though it can be minimised by careful processing. The entrapped air manifests itself as voids, which leads to a three-phase system in the syntactic foam structure. Another possible scenario of less wetting and penetration of the matrix towards the hollow spheres is observed, resulting in an empty space between the hollow spheres, and thus giving rise to voids in the system. Sometimes voids are intentionally incorporated by using a blowing agent to obtain lower density (John and Nair, 2010).

The two-phase syntactic foam, due to its closed-cell structures, offers excellent water-absorption resistance ability, thus leading to the use of this foam in applications which require both low density and hydrostatic compression strengths, such as deep submergence buoyancy materials. The three-phase syntactic foam as shown in Figure 2.4(b), however, has certain limitations compared to the two-phase system with respect to its mechanical properties due to the presence of voids. They possess excellent low dielectric and thermal loss properties.

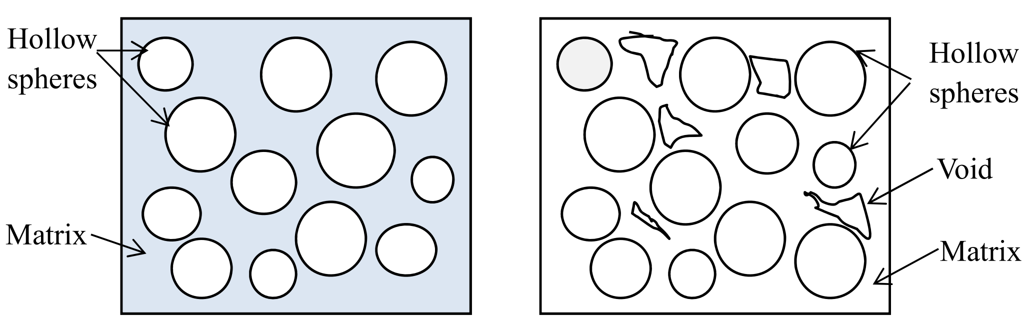

Figure 2.4: Schematic representation of the features in the (a) two-phase and (b) three-phase structures of the syntactic foam (Gupta and Ricci, 2006)

2.3 Parameters properties of the syntactic foam

The properties of the syntactic foam can be tailored for optimum performance. A wide variety of parameters can be changed, as reported in the previous studies, such as wall thickness and volume fraction of the hollow sphere materials, hollow sphere sizes, and size distribution (Gupta and Woldesenbet, 2004; Gupta and Ricci, 2006). The changing of these parameters has a significant effect on the physical and mechanical properties of the syntactic foam.

2.3.1 Wall thickness

Gupta and Woldesenbet (2004) have introduced the concept of the radius ratio, the η parameter, in order to establish a relationship of the radius ratio and the wall thickness of the hollow sphere,

$$\eta = \frac{r_{\mathrm{i}}}{r_{\mathrm{o}}} \tag{2.1}$$

where r_i is the internal radius and r_o is the outer radius of the hollow sphere. The wall thickness increases correspondingly when η decreases, leading to a contraction in the density of the hollow sphere. Similarly, hollow spheres with a higher value of the η result in lower density of the syntactic foam and vice versa (Gupta and Woldesenbet, 2004; Gupta and Ricci, 2006; Woldesenbet and Peter, 2009). It was theoretically established that the syntactic foam having η value higher than 0.71 experiences similar stress states in the specimen during compression testing, where the fracture of the hollow sphere has not induced any compression on the matrix. However, a fracture of the hollow sphere having an η value lower than 0.71 generates additional stresses in the matrix, thus leading to significant increase in the stress intensity in the compressible material (Gupta and Woldesenbet, 2004).

2.3.2 Volume fraction

The effects of variation in hollow sphere volume fractions of the physical and mechanical properties of the syntactic have been studied by many researchers (Gupta and Ricci, 2006; Porfiri and Gupta, 2009; Woldesenbet and Peter, 2009). They found that an increase in the volume fraction decreases the density and strength of the syntactic foam. It was reported that most applications tend to use syntactic foam having volume fraction in the range of 0.3 to 0.65. In this volume fraction range, most of the syntactic foam shows a stress-plateau in its compressive stress-strain curve, thus contributing to high energy absorption (Gupta and Ricci, 2006).

2.3.3 Hollow sphere size

The size of the hollow spheres has a strong effect on the mechanical properties of the syntactic foam. Wu (2007) and his co-workers examined the effects of the size in question on compressive strength. They found that smaller spheres contain fewer flaws in their microstructure than the larger ones, thus ensuring high compressive strength of the syntactic foam. Orbulov (2012) investigated the size effect of the ceramic and metallic hollow spheres in the metal matrix syntactic foams (MMSFs). A similar observation was made in the case when the smaller hollow