INNOVATIVE APPROACH FOR PRODUCTION OF EPOXY SYNTACTIC FOAMS CONSISTING OF EPOXY HOLLOW SPHERES

by

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LIST OF ABREVIATIONS

ASTM	American Society for Testing and Materials
$CaCO_3$	Calcium Carbonate
CO_2	Carbon Dioxide
$(CH_2COO)Ca_2$	Calcium acetate
CH_3COOH	Acetic Acid
DGEBA	Diglycidyl ether of Bisphenol A
DI	Deionized
DSC	Differential Scanning Calorimetry
EHS	Epoxy hollow sphere
EPS	Expanded Polystyrene
ESF	Epoxy Syntactic Foam
FGSF	Functionally Graded Syntactic Foam
ROV	Remotely Operated Vehicle
Temp	Temperature
TGA	Thermogravimetric analysis
TMD	Trimethylhexamethylene Diamine
3-D	3-Dimensional

LIST OF SYMBOLS

%	Percentage
cm	centimeter
mm	milimeter
kg/m^3	Kilogram per cubic meter
°C	Degree Celsius
MPa	Mega Pascal
r_i	Inner radius
r_o	Outer radius
ŋ	Radius ratio
g/cc	Gram per cubic centimeter
g/eq	Equivalent weight
mPa*s	Mili Pascal second
g/ml	Gram per millilitre
lbs/gal	Pound per gallon
mg KOH/g	Miligram potassium per gram
min	minute
g/l	Gram per liter
kg	kilogram
°C/min	Degree Celsius per minute
ρ	Density
W	Weight
V	Volume
Σ	Average

PENDEKATAN INOVATIF UNTUK PENGHASILAN BUSA SINTAKTIK EPOKSI MENGANDUNGI SFERA BERONGGA EPOKSI

ABSTRAK

Sfera epoksi berongga (EPS) telah difabrikasikan melalui teknik penyalutan berasaskan campuran epoksi/agen pematangan ke atas sfera terkembang polisterina pada formula nisbah epoksi: agen pematangan 1:0.5 (lebihan epoksi), 1:1(nisbah setara) dan 1:2 (lebihan amina) dan dicirikan melalu ujian Kalorimeter Imbasan Pembezaan (DSC), sifat luaran sfera dan ujian mampatan. Hasil ujian menunjukkan bahawa EPS pada nisbah 1:1 menghasilkan permukaan salutan yang licin dan struktur dinding yang kuat berdasarkan analisa pencirian pematangan menggunakan teknik DSC. Satu pendekatan inovatif melibatkan teknik bantuan vakum bagi penghasilan busa sintaktik daripada sfera epoksi berongga dan resin epoksi telah diperkenalkan untuk dibandingkan dengan busa sintaktik yang terhasil melalui teknik biasa; teknik tuangan acuan. Dalam kajian ini, spesimen yang dihasilkan telah dicirikan melalui ujian ketumpatan dan mampatan. Kesan teknik pemprosesan terhadap sifat spesimen busa sintaktik dianalisa melalui lengkuk tegasan-terikan dan corak kegagalan busa sintaktik yang telah diisi dengan EPS yang sama saiz. Teknik bantuan vakum telah berjaya mengurangkan jumlah rongga dalam matrik yang terhasil akibat teknik pemprosesan dan seterusnya meningkatkan kekuatan mampatan dan modulus. Spesimen yang dihasilkan menerusi teknik vakum tersebut telah dikaji dengan lebih lanjut dengan mempelbagaikan beberapa aspek iaitu saiz sel (BASF 403, BASF 303 dan B-normal) dan struktur dalaman EPS (dengan sokongan dan tanpa sokongan). Kesan orientasi ujian pemampatan ke atas corak kegagalan

spesimen juga telah dikaji untuk membantu dalam menjelaskan perbezaan lengkuk tegasan-terikan. Di bawah bebanan mampatan, kejadian kegagalan bermula apabila tekanan tertumpu pada sfera berongga yang paling lemah dan berpindah ke sfera bersebelahan dan mempamerkan dataran melalui dataran melintang yang lebih lebar. Apabila hampir kesemua sfera telah berjaya diruntuhkan, terdapat peningkatan tegasan yang mendadak pada lengkungan tegasan-terikan dan perkara ini menunjukkan bahawa, mekanisme kegagalan berlaku secara pemadatan seragam pada keseluruhan spesimen.

INNOVATIVE APPROACH FOR PRODUCTION OF TWO-PHASE EPOXY SYNTACTIC FOAMS CONSISTING EPOXY HOLLOW SPHERES

ABSTRACT

Epoxy spheres were fabricated via coating technique which utilized series of epoxy/curing agent mixture onto expanded polystyrene beads (EPS) formulated at ratio of 1:0.5 (epoxy rich), 1: 1(equivalent ratio) and 1:2 (amine rich) and their characteristic were investigated in term of differential scanning calorimeter (DSC), appearance and compressive behaviour. The results showed that EHS produced using epoxy/curing agent ratio of 1:1, exhibited smooth coating surface and yielded strong shell structure reflected from analysis of curing characteristic using DSC technique. An innovative approach involving vacuum assisted technique for preparation of syntactic foam made of epoxy hollow spheres and epoxy resin was introduced to be compared with syntactic foam produced through conventional technique; mold-casting technique. In this study, the resultant specimen was characterized for density and compression properties. Effect of different processing techniques on specimen was analysed through stress-strain curve and failure pattern of the syntactic foam filled EHS with the same EHS size. The vacuum assisted technique has successfully reduced voids within the matrix that was produced due to the processing technique and subsequently resulted in higher compressive strength and modulus. Specimen produced by the vacuum assisted technique was further investigated by varying several aspects in terms of cell sizes (BASF 403, BASF 303 and B-Normal) and internal structure of EHS (supported and unsupported). The effect of compression

test orientation on the specimen failure pattern was also examined to assist in explaining in stress-strain curve difference. Under compressive loading, the failure initiated when stress concentrated on the weakest epoxy spheres slowly propagated through adjacent spheres and displayed wider horizontal plateau. When almost all sphere have been successfully collapsed, there was a drastic increase in stress on the stress-strain curve and this indicated that failure mechanism occurred via uniform densification throughout the specimen.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Composite materials have been proven as one of the advanced materials offering superior properties across a wide range of disciplines replacing several numbers of traditional materials. Through the expansion of research activities, the understanding on the composite properties has been well emphasized and it has experienced growing trend in versatility of uses and applications which include severe applications that requires durability and endurance under extreme conditions, for instance aerospace applications, marine underwater vessels and ground vehicles.

Still, application of buoyancy aid materials for deep submergence equipment or vehicles involved had little success when it was made up from one single material to achieve high level performance materials. High compressive strength with low water absorption requirement in deep sea application while offering relatively low density is very critical. During that time, the conventional foamed materials did not reach requirement of compressive or shear strength to prevent implosion and water absorption through the interconnected cell chambers at high hydrostatic pressure encountered in these deep submergence applications (Lee and Lee, 1992).

Conventional foam offers weight reduction in structure with severe limitation in certain application that requires high strength and modulus (Gupta and Shunmugasamy, 2011). Also, in aerospace application, composite materials have been accepted as structural materials which are more efficient compared to metals. The manufacturer of helicopter previously used composite sandwich panel construction utilizing honeycomb core for a flatter structure. The conventional stabilized sandwich core reported lower compressive strength less than 10 MPa that caused a design problem to the aircraft sandwich panel design which experience high compressive loading.

As a countermeasure, new approach in development of this advanced material science has expanded multidisciplinary research activities via combining two or more conventional materials depending on properties of its constituents resulting in superior final composite properties with better strength-to-weight ratios known as syntactic foam. In 1960's, it was originally developed by introducing filler of light weight hollow microspheres distributed within the matrix called binder which yielded a specific type of foam called syntactic foam. Figure 1.1 shows several cross-section images of syntactic foams.

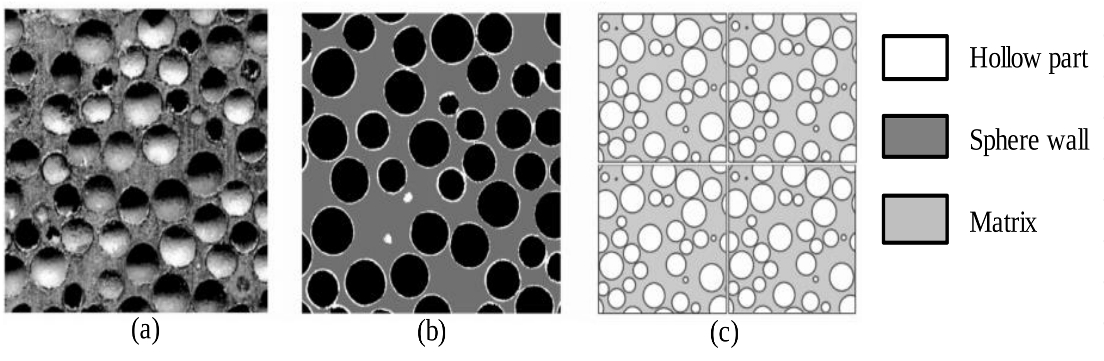

Figure 1.1: Cross sections of syntactic foams consisting of single-sized hollow spheres at random positions and matrix: a) photograph of real image b) computed tomography reconstruction, c) computer-generated models (Fiedler et al., 2008)

Figure 1.1 describes syntactic foam system consist of gas-containing particles that enclosed within the rigid walls of the microspheres dispersed in resinous matrix whereas distribution of microspheres often being random and the spheres are isolated from each other. Unlike conventional foam, syntactic foams demonstrate extremely high compressive strengths contributed by the resin matrix and the hollow spheres. Present studies affirmed that syntactic foams with lower density retained higher modulus than the conventional matrix in polymer matrix materials (Gupta and Shunmugasamy, 2011). The microspheres encapsulated air/gas voids within the shells of the microspheres offering lightweight, high stiffness and thermal stability in potential applications such as aerospace application and submarine application. The rigid shells of the closed pore structures as presented in Figure 1.2 are considered to be stiffer and stronger than open cell structures in conventional foams making them attractive for structural applications.

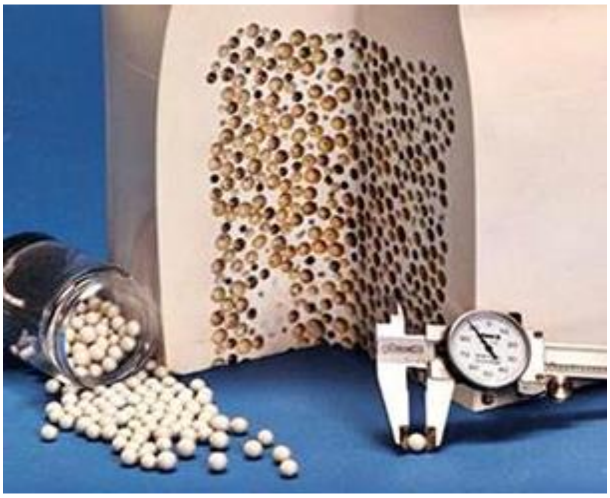

Figure 1.2: Syntactic foam embedded with reinforced composite spheres (Boivin, 2014)

Specifically, materials that are frequently selected as matrices comprise of epoxy and phenolic resins, polyesters, silicones, polyurethanes and several available polymers while the microspheres have been made of carbon, metal, ceramics, glass, and polymers. An example of polymer spheres in various sizes given in Figure 1.3. The microspheres are characterized corresponding to the particle sizes, wall thickness and density that possess significant resistance to damage when force is imposed during formulation, mixing and dispending process.

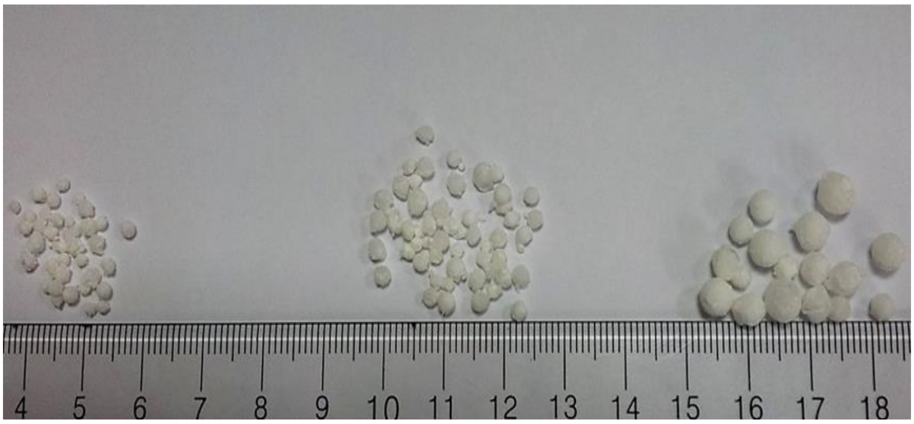

Figure 1.3: Several different sizes of EHS ranging in centimeters

At present, research activities have been focused on the fabricating hollow polymer microspheres yet few processes and techniques was successfully manufactured but still fewer achieve commercial application. Various techniques and strategies have been established for fabricating hollow microspheres in such liquid droplet, dried–gel droplet, self-assembly method, microencapsulation, emulsion polymerization and template method have been reported (Wei et al., 2009).

Importantly, it is necessarily to overcome complex fabrication processes while challenge time-consumption during production in future research**.** Epoxy spheres produced via coating technique have been explored in this study offers great advantage through utilization of conventional material while still providing equivalent properties compared to other hollow spheres available in industry. In-house fabrication technique of the spheres is proposed providing better ability to be cheaply mass produced and it is estimated that the fabricated spheres are able to give effective structural support due to its matching shell characteristics with the resinous epoxy matrix. The produced epoxy spheres are basically made of expandable polystyrene coated-epoxy having the capability to retain high compressive strength, lightweight and spherical shape tends to have the least surface for a given volume compared to any other shape. By tailoring the binder-to-hollow spheres ratio, volume fraction, shell thickness and material of polymer hollow spheres embedded in matrix, numerous properties can be tailored and made available in diverse range of application.

1.2 Problem Statement

Glass and carbon are normally favored as hollow spheres constituent in syntactic foam for the last decades. Carbon mostly chosen as hollow spheres due to its numerous properties in such higher thermal and electrical properties while promising lower density, which make its more appealing than glass in certain applications (Carlisle et al., 2006). Furthermore, severe limitation notify when utilizes glass hollow spheres as constituent in syntactic foam usually show solubility effects under extreme conditions (Wang, 2002).

Certainly, microspheres made up from the organic materials suffers from many limitation which can be easily transformed into carbon microspheres when it experienced heating in an inert atmospheres to 800^{o}C to 1000^{o}C. Due to some limitation in its applications fields, polymeric microspheres have been explored and numerous polymeric spheres have been successfully manufactured such as from epoxy resin, unsaturated polyester resin, silicone resin, phenolic, polyvinyl chloride, polypropylene and polystyrene (John and Nair, 2010) . The idea of fabricating in-house polymeric spheres is revealed by introducing epoxy spheres via coating technique of expandable polystyrene beads. The major aim of this work is to develop polymer hollow spheres by tuning appropriate choice of the resin system formulation because it can impart the macromolecular networks from within the shell thus affecting on the epoxy hollow spheres performances.

Currently, there have been several researches conducted in fabricating epoxy hollow spheres (Samsudin et al., 2011) however in this study; expandable polystyrene foam beads will be used as the core or the template material and in some instances heat treatment will be used to create the inner hollow cell structure. The shape of epoxy hollow spheres tend to collapse its structure when coating surface not fully cured while core structure undergo decomposition in order to attain hollow part. The research will be focused on the production of epoxy spheres with different internal structures and its corresponding effects towards performance of the syntactic foam. Failure mechanism under compression will be discussed in term of individual epoxy spheres by varying the internal structure of epoxy spheres used in prepared syntactic foams. The fracture behavior of epoxy spheres in epoxy syntactic foam is one of the areas that uncertainly need to be clarified. This behavior have not precisely been understood and yet to be explored. Besides, failure behavior also will be examined to construct better understanding on failure pattern of syntactic foam affecting from variation of epoxy hollow spheres sizes ranging from 1 mm to 8 mm.