SILICONE MICROSPHERE FILLED SYNTACTIC FOAM

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DATE: (DEEPIKA CHAUHAN)

DECLARATION

I DEEPIKA CHAUHAN hereby declares that the thesis entitled **"SILICONE Microsphere Filled Syntactic Foam"** is an authentic record of research work done by me under the supervision of **Dr Prasun K. Roy** Scientiest 'E' Centre For Fire Explosive and Fire Safety (CFEES) Defense Research Development Organization (DRDO) and **Dr. D. Kumar,** Professor Delhi Technological University, Delhi. This work has not been previously submitted for the award of any degree or diploma of this or any other University/Institute.

Date: Deepika Chauhan

M.Tech (Polymer Technology)

(2K14/PTE/03)

ABSTRACT

Highly damage tolerant hybrid syntactic foams are developed by using polydimethylesiloxane (PDMS) particles to modify the matrix microstructure in syntactic foams. Two different types of glass hollow particles (microballoons) with different densities are used to fabricate the foam samples. In this study, the effect of PDMS particle size (45µm, -200µm) at different volume fractions (3%, 5%, 7%and 10%) is being studied. First the volume content of filler is being optimized. The total volume of fillers is maintained at 40% in plain and hybrid syntactic foams. The plain and hybrid syntactic foams are characterized for mechanical properties. An increase in toughness is observed with the incorporation of PDMS in syntactic foams. The strength of micro balloons plays an important role in determining the fracture mode of plain and hybrid syntactic foams. Silicon microspheres are found to increase the energy absorption under the flexural loading conditions.

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CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

A Large number of studies is found published on the use of glass microspheres in syntactic foams [1, 2] and carbon nanofibre, crumped rubber particle and nanoclay reinforced syntactic foams [3, 4]. Various processing techniques have been developed by researchers for the fabrication of reinforced syntactic foams[5]. Techniques developed in these studies have been used in the present study to achieve minimal air entrapment and appropriate wetting of microballoons, fillers and resin so that void content is reduced and a strong resin-microballoons interface is obtained.

Hollow particle filled composites materials, called syntactic foams, are primarily used in marine and aerospace applications, which require high compression and flexural properties of materials. Syntactic foams containing low density microballoons have the advantage of lower weight and high fracture strain under compression; however they have low compressive strength [1,2].

The compressive strength of the syntactic foams can be improved by using high density or high strength microballoons. It is known that the fracture toughness and ductility of polymers can be increased by the addition of rubber particles [10–14]. Fracture strain and compressive toughness of syntactic foams have been found to increase due to the addition of rubber particles in a polymeric matrix, with only a very small reduction in their strength [8]. The increase inductility of the material is attributed to the plasticizing effect of rubber, crack deflection at the rubber particles and cavitation on the polymer resin matrix [15].

The present work is focused on characterizing the flexural properties of these hybrid syntactic foams. The studies on flexural properties of syntactic foams have included three-point bend, four-point bend, and short beam shear tests of the syntactic foams. Flexural modulus has been observed to increase with increase in the microballoons volume fraction in the material [20].

It is found that in sandwich configuration the flexural properties are mainly governed by the choice of skins [21].In the present study, an approach of modifying the resin matrix by addition of filler particles is adopted, in order to attain better flexural properties. Two variants of four-phase hybrid syntactic foams are developed and studied for flexural properties. Apart from resin and two types of particles these foams contain some air entrapped in the mechanical mixing process. This entrapped air causes open cell porosity, termed as voids, and is present as the fourth phase. A total of 18 types of syntactic foams are fabricated and their flexural properties are studied in three point bend configurations. Material stiffness, flexural strength and fracture strain are calculated and compared for different types of hybrid foams and plain syntactic foams.

1.1.1 Syntactic foams

Syntactic word is derived from Greek word *syntaktikos* meaning "to arrange together". The term 'foam' is used because of the cellular nature of the material.

Syntactic foams are physical foams in which foaming is achieved by the addition of hollow microspheres made up of polymers, glass or metals. ASTM defines it as "a material consisting of hollow sphere fillers in a resin matrix"[9]. They are lightweight materials with low density, high specific strength targeted for the use in marine, aerospace and such areas where weight is constraint. They are also known as foam composites since the hollow spheres can be regarded as reinforcements in polymer matrix. Syntactic foams, also known as foam composites are now a

day's widely being used as a replacement of heavy materials with no compromise in their mechanical properties when compared to their heavier counterparts. Regardless of the above fact that they find themselves suitable to a wide range of applications designed especially for them. Beyond the limits of the sky to the depths of the ocean there is no such area where they cannot apply themselves to. The aircrafts nowadays require lightweight materials without compromising on the stringent requirements as far as the safety is concerned and so are the underwater jets and submarines which requires help in order to counterbalance their own weight, derive immense help from these novel syntactic foams. Foams, as they are called, consist of hollow spaces or voids in between the matrix which plays a crucial role in providing the foams their uniqueness. Generally they are tertiary systems comprising of matrix, hollow microspheres and sometimes voids also adding to their structure.

1.1.2 Matrices used in Syntactic Foams

The matrices used in syntactic foam include polymer[10], metal[11] or ceramics. Thermoplastic and thermosetting polymers have been employed to fabricate syntactic foams. The important thermosetting resins used are epoxies[12], phenolics[13], vinyl esters[14], bismaleimides[14], unsaturated polyesters, and polyurethane[15]. Examples of thermoplastic resin matrices used include polyethylene, polystyrene, polypropylene[16], and nylons. Syntactic foams are mainly prepared by using thermosetting matrices because of the favourable processing conditions, i.e., avoiding breakage by gently blending the hollow microspheres with thermosets precursors of very low viscosity. From the processing viewpoint, thermosetting syntactic foams have many advantages over the thermoplastic ones. For example, thermosetting syntactic foams can be processed at much lower temperatures compared with 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. 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.

1.1.3 Microspheres Used In Syntactic Foams

A hollow microsphere gives the syntactic foam its low density, high specific strength, and low moisture absorption. Microspheres may comprise glass[17], polymer, carbon[13], ceramic[11], or even metal. Bio based reinforcements are now being chosen as opposed to polymeric materials. Shah, D. U., F. Vollrath, et al.demonstrated the use of silk cocoons as a natural microballoons filler in polyurethane foams[18].Other terminologies are used in the literature to describe microspheres (e.g., microballoons, cenospheres). All these terms are intermittently used throughout to indicate hollow microspheres. The microspheres have a burst pressure sufficient to withstand the forces imposed upon them during the formulation, mixing and dispensing processes. Because of the Properties such as high temperature resistance, good strength-to-weight ratios, low thermal conductivity, clean surface chemistry and low dissipation factor make microballoons an important reinforcing material in these composites.

1.1.4 Structure of Syntactic Foams

Syntactic foams are usually tertiary systems because the matrix and microspheres are usually composed of different materials. They are classified as two-phase systems and three-phase systems. 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 1.1(a). During the processing of syntactic foams, air entrapment is possible, which leads to voids in the foam

structure. In some other cases, a thin film of resin may surround the cluster of microballoons so that the resin cannot penetrate into the cluster, leaving an empty space in between the microspheres. Sometimes, depending upon the application, voids are intentionally incorporated to obtain lower density. The existence of voids makes syntactic foams a three-phase system (unlike conventional polymer foams which are binary). The three-phase structure is shown schematically in Figure 1.1(b). Thus, two-phase syntactic foams consist of hollow microspheres dispersed in a resin, whereas three-phase syntactic foams comprise hollow microspheres dispersed in a resin containing finely dispersed air bubbles.

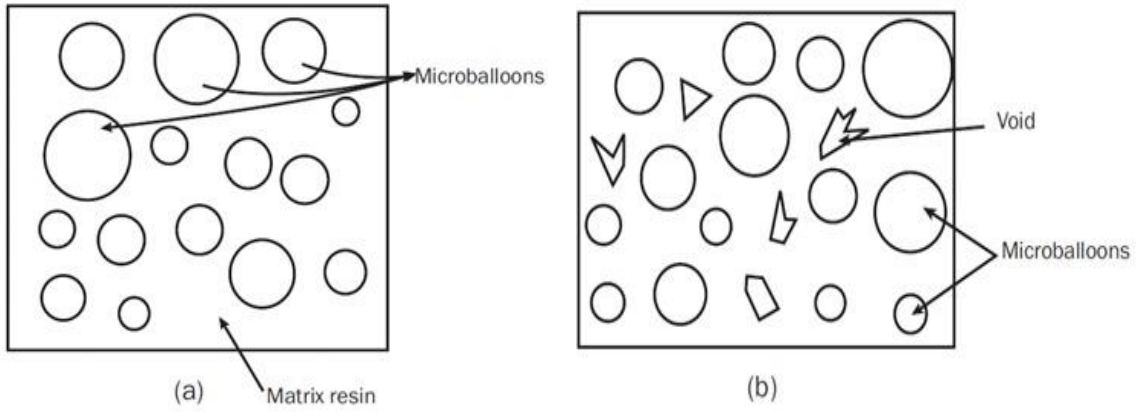


Fig 1.1: Schematic representation of (a) two-phase and (b) three-phase structures of syntactic foam.[9]

1.2 Epoxy syntactic foam

The properties of syntactic foams are dependent on the nature of polymer matrix, concentration of matrix, type of the curing agents and type of the microballoons used. Epoxy resins are one of the most commonly used matrix because it can produce a syntactic foam which can be easily formulated in various ways to give the desired end product with higher strength and stiffness ,thermal and environmental stability, creep resistance and lower shrinkage and water resistance

respectively. Epoxy resin with different variety of microballoons has been used to process syntactic foams. Epoxy syntactic foams with glass polystyrene, carbon, phenolics, and mineral microballoons have been reported.

1.2.1 Thermosetting epoxy resins

Epoxy resins are one of the most important classes of thermosetting polymers. The resin network has many desirable properties which include high tensile strength, excellent chemical and corrosion resistance and good dimensional stability [19, 20]. As a result, these materials are widely used for the applications such as matrix for syntactic foams and advanced composite material [23-25]. Polyepoxide, known commonly as “epoxy” is a thermosetting polymer formed as a result of the reaction between an epoxide "resin" with polyamine "hardener". Commercial epoxy resins contain aliphatic, cycloaliphatic and aromatic backbones. They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peracids. The most important intermediate for epoxy resins is the diglycidyl ether of bisphenol A (DGEBA), which is synthesized from bisphenol A and excess epichlorohydrin as per shown in the fig 1.2.

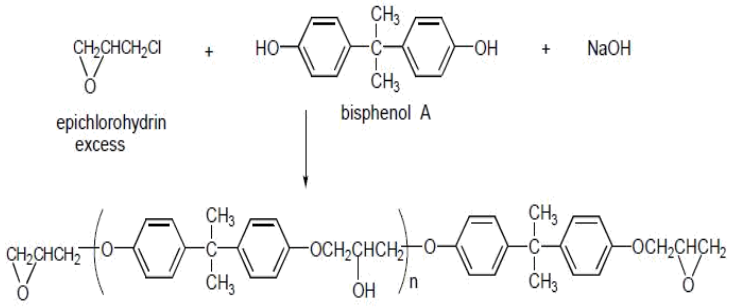


Figure1.2: Synthesis of diglycidyl ether of bisphenol A (DGEBA)

The epoxide ring can react with chemicals with different structure, especially those, have activated hydrogen atom such as alcohols, amines and carboxylic acids, to mention a few. Treatment of epoxy resins with these agents results in formation of three dimensionally insoluble

and infusible networks. The choice of curing agents depends on the required physical and chemical properties, processing methods and curing conditions which are desired. Epoxy resins can be cured with either catalytic or co-reactive curing agents who function as initiators for epoxy ring- opening homo-polymerization.

Among chemicals which have the potential to act as curing agents, the primary and secondary amines are the ones which are most commonly employed. Primary amine functionality reacts with an epoxy group to produce a secondary amine and a secondary alcohol. The secondary amine can further react with an epoxy group to form a tertiary amine. Commercial hardeners generally consist of polyamine monomers, a typical example being triethylenetetramine (TETA). Each amine functionality can react with an epoxide group, so that the resulting polymer is heavily cross linked, and results in a formation of a rigid and strong structure. For the present study, a cycloaliphatic epoxy resin was chosen due to its potential applicability in different areas and more importantly its UV stability, in view of the absence of light absorbing phenyl rings.

A reaction scheme representing the reaction between the primary amine functionality of TETA with epoxy group is shown in figure 2.This process is also referred to as "curing", and can be controlled through proper choice of temperature, type of resin and hardener, and the ratio of said compounds. The curing process, which is exothermic in nature, can take minutes to hours for completion. Some formulations benefits from heating during the cure period, whereas others require time and ambient temperatures.

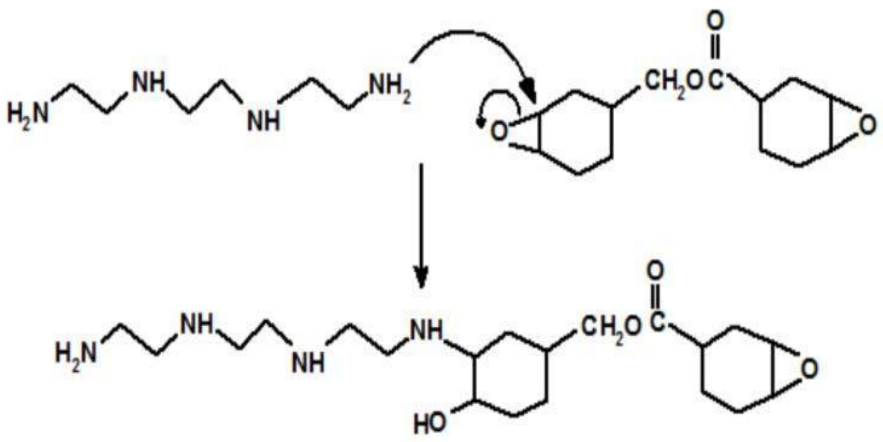


Figure 1.3: Reaction scheme of primary amine of TETA with epoxy group of cycloaliphatic epoxy resin

1.3 Rubber Particle Filled Syntactic Foam

An effective way of toughening epoxies is to add rubber particles. Evidently, the rubber particles can absorb more impact energy through elastic deformation of the particles, leading to higher toughness of the matrix. In addition, the lower stiffness rubber particles serve as stress concentrators. Once the stress exceeds the strength of the materials, microcracks will initiate. Accompanying the creation of microcracks, a considerable amount of impact energy will be consumed, resulting in higher energy absorption capacity. However, these microcracks will not easily develop into macrocracks. 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 provides a way of absorbing impact energy; it also provides a mechanism of preventing the microcracks from developing into macrocracks or catastrophic structural failure. Crumped rubber particle is being studied till now, silicone microsphere filled syntactic foam is new idea that is being studied in this report.

1.4 Applications of Syntactic Foam

Syntactic foams are finding applications in fields that are as diverse as deep sea vehicles, space vehicles, aircraft, snow skis, soccer balls and thermal insulation in under water pipelines. Based on the properties, application of syntactic foams can be divided into three categories which are given below.

1.4.1 Compressive properties

Syntactic foams are lightweight porous composites that are made by incorporation of HGMs while keeping the compressive strength high as the stiffness of glass microsphere is high which makes it load bearing element under compression. Because of hydrostatic compression encountered by submarine and under water unmanned vehicles, the properties of syntactic foams are effectively used here. The National Oceanic and Atmospheric Administration (NOAA) uses Advin and Janson underwater vehicles such as Human Occupied Vehicle(HOVs) [30], Remotely operated vehicles(ROVs), Autonomous underwater vehicles(AUVs) that are made of syntactic foams to withstand the extreme pressure thousands of meter below the ocean surface for the purpose of deep sea exploration. The Deep Sea Challenger, used by James Cameron for the exploration of Mariana Trench, was made of reinforced syntactic foam. The syntactic foam structure of the HOVs, ROVs and Challenger craft as shown in figure

Fig: 1.4 HOVAlvin and ROVs Jansonused for deep see exploration**.** Photo courtesy (NOAA)

1.4.2 Thermal insulation

The incorporation of HGM in syntactic foams produces 30-50 vol% voids in syntactic foams. The uniformly distributed voids pockets and insulating nature of epoxy matrix provide insulating properties to syntactic foams. These materials provide insulation for deep sea oil and gas pipelines. External fuel tanks used in space vehicles are also made of syntactic foams which provide thermal insulation in space.

1.4.3 Dimensional stability and low coefficient of thermal expansion

Syntactic foams are used as composite material tooling boards and plug assists because of their high thermal stability and low CTE. Low CTE of tooling leads to only small dimensional changes and distortions as the temperature changes during composite fabrication for reason such as exothermic curing temperature. Low CTE of syntactic foams has been useful in developing space mirrors that maintain dimensional stability during rapid and large temperature changes. [16]

1.5 Aims and Objectives

This project deals with a novel approach to fabricate PDMS microspheres modified syntactic foams using different densities glass microballoons (K15 & K46) and silicone microspheres at varying volume fractions and their effect on mechanical properties is being studied.

A systematic methodology highlighting the progress of the proposed work involves following steps:

- Preparation of syntactic foam using different density glass microballoons.
- Studying the effect of varying volume fraction on mechanical properties (impact, flexural and compression) of the composites.
- Fabrication and characterization of PDMS microspheres particle.
- Studying the effect of PDMS microspheres of different density and at varying volume fractions on the flexural properties of syntactic foams.

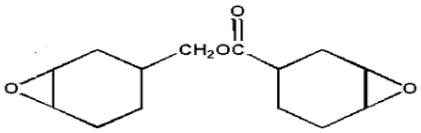
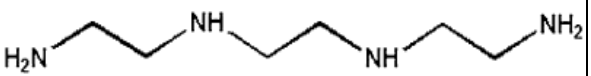
CHAPTER 2

EXPERIMENTAL

2.1. Materials

Cycloaliphatic epoxy resin (Ciba Geigy, Araldite CY 230; epoxy equivalent 200 eq g^{-1}), hardener (HY 951; amine content 24 eq kg^{-1}) and Hollow glass microballoons (K15 & K46 3M) were used as materials for preparation of syntactic foam.Microballoons were kindly supplied by Chemtech Specialty, Mumbai. Silicone resin (ElastosilM4644) and the platinum based hardener was obtained from Wacker, Germany. PVA (Mol. wt. 14000, CDH) and chloroform (CDH) were used without any further purification. Double distilled water was used throughout the course of study.

Table 2.1: Properties of epoxy and TETA

Grade	Structure	Epoxy equivalent
CY 230		200 eq/g
HY951		Amine equivalent 32 eq/kg

2.2 Glass microballoons

The glass microballoons used in the present study are hollow glass microspheres, which are being increasingly used for many demanding applications where weight reduction, lower costs and enhanced product properties are desired. They are chemically stable soda- lime-borosilicate glass and possess excellent water resistance to create more stable emulsions, they are also non-combustible and non porous so that they do not absorb resin. The microballoons used are manufactured by 3M and kindly supplied by Chemtech Speciality. Physical properties of these microballoons are presented in table 2.1

Table 2.2: Properties of Microballoons

Microballoons Type	**Average true particle Density (kg/m^3)**	**Isostatic Crush Strength (psi)**	**Ri/Ro**	**Wall thickness (µm)**	**Mean particle size (µm)**	**Thermal Conductivity ($W\text{-}M^{-1}K^{-1}$)at21° C**
K15	150	300	0.95	0.7	60	0.055
K46	460	6000	0.9356	1.29	40	0.153

2.3 Preparation of elastomeric microspheres

The PDMS microspheres are prepared by suspension polymerization process. A feed solution is prepared by diluting vinyl terminated siloxane macromonomer with the chloroform (30–60 % w/v) followed by the addition of requisite amounts of platinum based hardener. The curing reaction is being performed in reaction vessel under inert atmosphere condition where the feed was introduced through a hypodermic syringe into an aqueous PVA solution (1.5 % w/v), which

is being maintained at 45 °C under continuous stirring. The polymerisation reaction was allowed to continue for 8 h under varying stirring speed (1300 - 1500 rpm), after which the reaction mixture is being allowed to cool and filtered. The extent of conversion is measured gravimetrically as the ratio of mass of microspheres obtained to the amount of macromonomer used for its preparation. The obtained microspheres of varying size are being separated using series of sieve.

2.4 Fabrication of syntactic foam

Neat syntactic foams were prepared first by adding 40, 50 and 60 volume fractions of HGM (hollow glass microballoons) respectively in epoxy matrix. The contents were mixed thoroughly and degassed to remove entrapped voids. Next 13 phr hardener was added to the above formulation and the resulting composition was transferred to silicone mould. The samples were cured at room temperature for 24 hours**.** Silicone microspheres filled syntactic foams are fabricated by adding different volume fractions of rubber particles in 40 vol percent syntactic foams. Addition of the amount of silicone microsphere will lead to the replacement of glass microspheres. In silicone modified syntactic foams, silicone microspheres are initially mixed with glass microspheres and then added into epoxy matrix. . The contents were mixed thoroughly and degassed to remove entrapped voids. Next 13 phr hardener was added to the above formulation and the resulting composition was transferred to silicone mould. The samples were cured at room temperature for 24 hours**.**

Table 2.3: Compositions and Designation of Syntactic Foams

Sample Code	Matrix (% v/v)	Microballoons(% v/v)	Microballoons(%wt)
K15_SF40	60	40	7.80
K15_SF50	50	50	11.36
K15_SF60	40	60	16.13
K46_SF40	60	40	20.76
K46_SF50	50	50	28.22
K46_SF60	40	60	37.09

Table 2.4: Compositions and Designation of PDMS Modified Syntactic Foams

Sample Code	Matrix (% v/v)	Microballoons(% v/v)	Silicone microspheres(v/v)
K15_PDMS3	60	37	3
K15_PDMS5	60	35	5
K15_PDMS7	60	33	7
K15_PDMS10	60	30	10
K46_PDMS3	60	37	3
K46_PDMS5	60	35	5
K46_PDMS7	60	33	7
K46_PDMS10	60	30	10

The actual amount of HGM was calculated as per the formula

$$\frac{Weight\ of\ HGM}{Weight\ of\ composite} = \frac{\rho_{HGM} \times \Phi_{HGM}}{\rho_{HGM} \times \Phi_{HGM} + \rho_{matrix} \times \Phi_{matrix} + \rho_{PDMS} \times \Phi_{PDMS}}$$

Where ρ_{HGM}, ρ_{PDMS} , and ρ_{matrix} refer to the density of HGM (0.15 g cc^{-1}, 0.46 g cc^{-1}), PDMS (0.965g cc^{-1}) and epoxy resin (1.17 g cc^{-1}) respectively and Φ_{HGM}, Φ_{PDMS} and Φ_{epoxy} refer to the desired volume fraction of HGM , PDMS and epoxy resin.

2.5 Density Determination

Theoretical density of syntactic foam (ρ_{th}) was calculated using standard rule of the mixture.

$$\rho_{th} = \rho_{PDMS} * \Phi_{PDMS} + \rho_{HGM} * \Phi_{HGM} + \rho_{matrix} * \Phi_{matrix}$$

Here,ρ andϕ represent density and volume fraction, respectively. For calculation purposes, ρ_{PDMS} has been assumed to be 0.965 g/cc. The density of hollow glass microballoons K15 and K46 has been reported to be 0.15g/cc and 0.46g/cc respectively. The density of epoxy was experimentally determined to be 1.17 g/cc.

2.5.1 Void Volume

The theoretical and experimental density $\boldsymbol{\rho_{ex}}$ values are compared and the air void porosity trapped in the matrix during fabrication was calculated as per the following equation:

$$Void\ volume\ \% = \frac{\rho_{th} - \rho_{ex}}{\rho_{th}} \times 100$$

Experimental density was calculated as weight of the sample to the volume of the sample measured experimentally.

2.6 Characterization of PDMS

2.6.1. Structural characterization

2.6.1.1 Scanning Electron Microscopy

The surface morphology and size of PDMS was studied using a Scanning Electron Microscope (Zeiss EVO MA15) under an acceleration voltage of 20 kV. The morphology of the silicone microspheres were carefully examined which were mounted on aluminium stubs and sputter-coated with gold and palladium (10 nm) using a sputter coater (Quorum-SC7620) operating at 10-12 mA for 120 s.

Principle:

Accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structure and orientation of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathode luminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

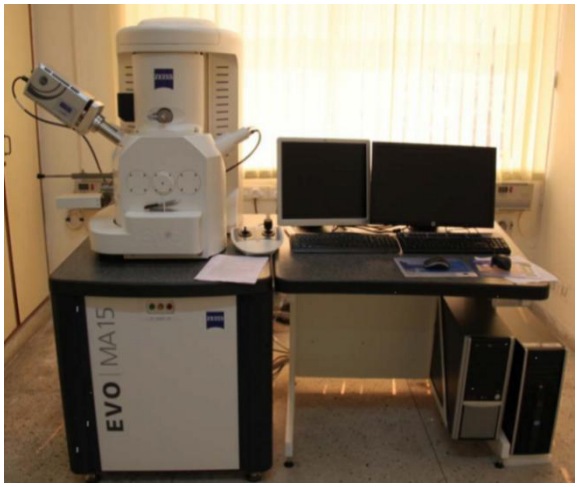


Fig 2.1: Scanning Electron Microscope

2.6.2. Thermal Characterization

2.6.2.1. Thermo Gravimetric Analysis

Thermal behavior of neat as well as PDMS loaded epoxy syntactic foams was investigated using Perkin Elmer Diamond STG-DTA under N_2 atmosphere in the temperature range 50-700 °C. A heating rate of 10 °C min^{-1} and sample mass of 5.0 ± 0.5 mg was used for each experiment

Fig 2.2: Thermogravimetric Analysis

Principal

Thermo gravimetric analysis (TGA) is based on the principle of the measurement of mass loss of material as a function of temperature. In thermo gravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. A plot of mass change versus temperature (T) is referred to as the thermo gravimetric curve (TG curve).

2.7 Mechanical Characterization

Mechanical properties of the polymers are of great interest to scientist and relevant to the industry. In order to fully understand the constitutive behaviour of these materials, the deformation properties of materials at quasi static strain rates must be quantified. Neat syntactic foams were subjected to mechanical tests and the results are displayed in the result section.

2.7.1 Compression Testing

Samples ($25\text{mm} \times 25\text{mm} \times 12.5\text{mm}$)were prepared and tested as per ASTM (C365-94) standard [17]. Three specimens of each type of reinforced syntactic foams are tested under a constant compression rate of 1.3 mm/min. Load displacement data is obtained in the tests and converted to stress-strain information to calculate compressive strength and modulus of hybrid syntactic foams.

2.7.2 Flexural Testing

Unnotched flexural testing of the samples was performed under three point bending mode as per ASTM D790. For this purpose, specimens of requisite dimensions (127 mm length x 12 mm width x 3.5 mm thickness) were prepared and subjected to a deformation rate of 2 mm/min while maintaining 60 mm span length. The samples were tested on Instron 3369 machine with a 50 kN load cell.

2.8 PDMS reinforced syntactic foams

Varying volume percentages of PDMS was dispersed in epoxy resin and samples so obtained were subjected to flexural testing.

Particle Size Analysis

PDMS microspheres hence obtained were segregated in to three different particle size of 200 microns, 125microns, 63 microns, and 45 microns using sieving method. The yields of different sizes of PDMS microspheres obtained by sieving process are reported in the results section.

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CHAPTER 3:

RESULTS AND DISCUSSION

This section deals with the characterization of PDMS microspheres followed by mechanical test results of neat as well as PDMS reinforced syntactic foams. The results of thermal studies are also included in this section.

3.1. Syntactic foams

Experimental and theoretical densities of syntactic foams along with the voids associated with different compositions are presented in Table 3.1 and Figure 3.1. As expected, increase in microballoons loading, led to a decrease in the density of the samples. For the sake of brevity, only PDMS microspheres added to K46 syntactic foams are presented in the table.

Table 3.1: Density Computation of K46 Epoxy Syntactic Foams

Sample	Theoretical density (kgm^{-3})	Experimental density (kgm^{-3})	Voids (vol %)
SF40	886	775.6	12.4
SF40_PDMS3	901.1	837.9	7.0
SF40_PDMS5	911.2	846.8	7.0
SF40_PDMS7	921.3	877.5	4.7

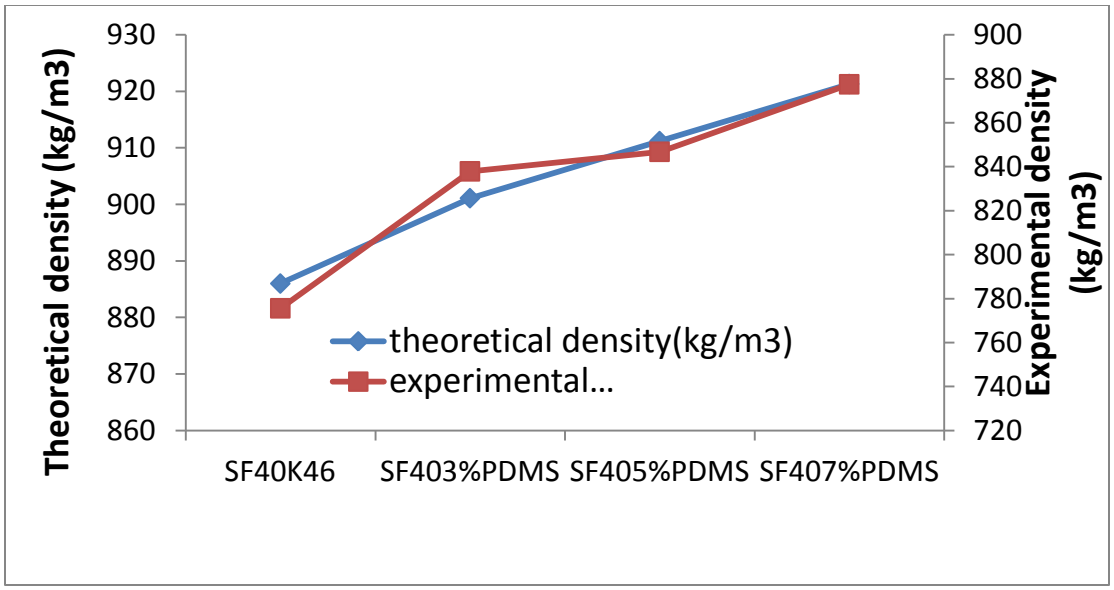

Fig 3.1: Theoretical and experimental densities of neat and PDMS loaded syntactic foams containing K46 microballoons only

3.2 Mechanical Testing of Neat Syntactic Foams

3.2.1 Compressive Test

The behaviour of neat syntactic foams containing K15 and K46 microballoons separately under compressive loadings was quantified using UTM and the variation with increasing loading is presented in Figure 3.2. In comparison to syntactic foams prepared using K15, the improvement in the compression strength of K46 containing syntactic foams was relatively larger, which could be attributed to large differences in the shell wall thickness of K46 and K15. However, their compression strength is much lower as compared to neat epoxy (138 MPa ± 5MPa).

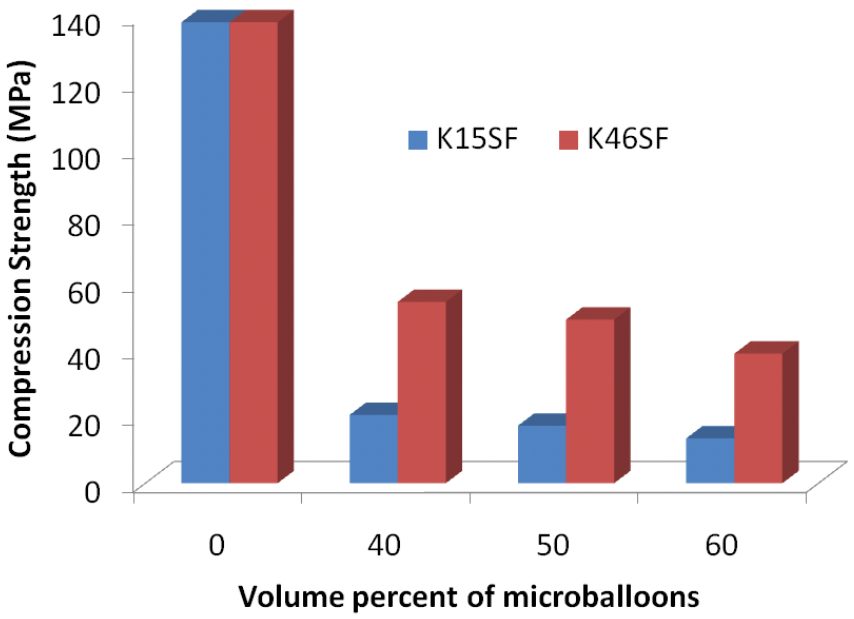

Fig 3.2: Compression yield strength of syntactic foams at different microballoons loading

3.2.2Tensile Test

The tensile strength of syntactic foams is primarily dependent upon the matrix material used and independent of the type of microballoons employed for its processing. In comparison to compression strength, the effect of microballoons loading on the tensile strength is relatively lesser as can be seen in Figure 3.3. It can be seen that there is a little difference between the tensile strength values of syntactic foams prepared using different densities of glass microballoons.

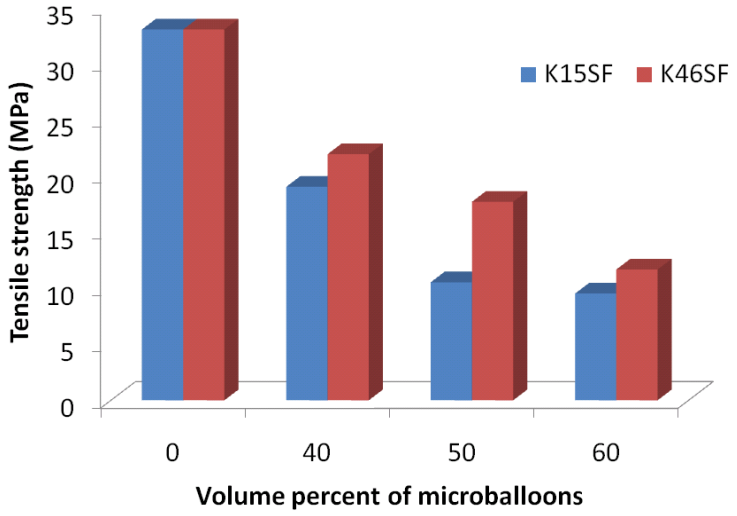

Fig. 3.3: Tensile yield strength of neat syntactic foams at different microballoons loadings

3.2.3 Flexural Test

The flexural strength of syntactic foams containing glass microballoons are presented in figure 3.4. The flexural test being a combination of both tensile and compressive tests, the flexural properties are dependent on the properties of both microballoons as well as the matrix material. The flexural strength of K46 microballoons containing epoxy syntactic foams is higher than those containing K15 HGM.

The mechanical properties of neat foams prepared using K46 HGM is far superior than foams prepared using K15 microballoons. Therefore, further studies are focussed on using K46 HGM syntactic foams. Moreover, from the above figures it can be inferred that as the microballoons loading increases, the strength of foams decreases. In view of this, epoxy syntactic foam containing K46 HGM at 40 % (v/v) was chosen as the representative system.

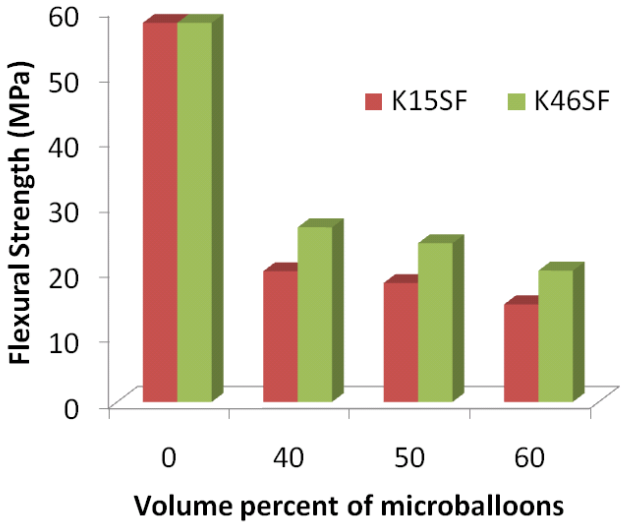

Fig 3.4.: Flexural yield strength of neat syntactic foams at different microballoons loading

3.3 Preparation and characterization of PDMS

In this study, a simple procedure for preparation of siloxane microspheres has been developed which have been subsequently employed as fillers in syntactic foams.

3.3.1 Suspension curing of siloxane

In the present study, vinyl terminated methyl hydro-siloxanedimethylsiloxane copolymer was cured at 45 °C in the presence of a hydrosilylation catalyst as per figure 3.5. The effect of varying the stirring speed on the particle size distribution of the microspheres is presented in Fig. 3.6, where the feed concentration was maintained at 60 % w/v. It was seen that with increase in the stirring speed (1300-1500 rpm), the particle size distribution shifts towards lower size, which could be attributed to the shearing of the large oily droplets into smaller microspheres, under the experimental conditions employed.

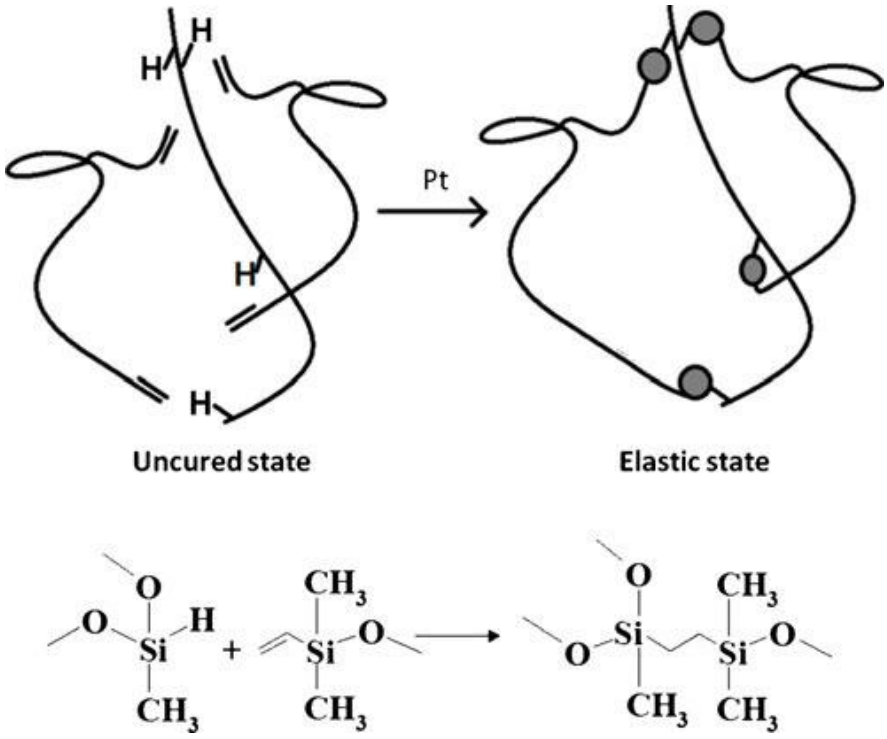

Fig 3.5: Platinum catalysed hydrosilylation of silicone

The amount of PDMS microspheres of different sizes as obtained by seiving was quantified in terms of yield as shown in table 3.2.

Table 3.2: Particle Size and PDMS yield %

Particle size	**Yield (%)**
200-125 µm	46.75
125-63 µm	34.50
63-45 µm	12.41
Less than 45 µm	6.34

3.4 Flexural properties of PDMS Loaded Syntactic Foams

Flexural properties of PDMD hybrid syntactic foam, flexural strength and flexural strain are represented in fig.3.6 and fig 3.7 at varying volume fractions of PDMS particle of the size range of 45- 200 µm. The effect of adding PDMS microspheres on the flexural properties of syntactic foam was studied and improvements in terms of strain percent and toughness were quantified. Brittle behaviour is evident in all the samples under flexural loadings. The results indicate that on adding silicone microspheres to epoxy matrix, there is a small decrease in the flexural strength of PDMS loaded samples compared to neat variety. This can be attributed to the fact addition of soft and flexible phase decreases the strength of the overall composites. However significant improvements in terms of strain percent and toughness were observed in all PDMS reinforced specimen. The presence of a soft rubbery phase increased the fracture strain which in turn led to a substantial increase in the toughness of the composites. A maximum increase of 32 percent was observed at 5 percent loading of PDMS

3.4.1 Flexural Strength and Strain

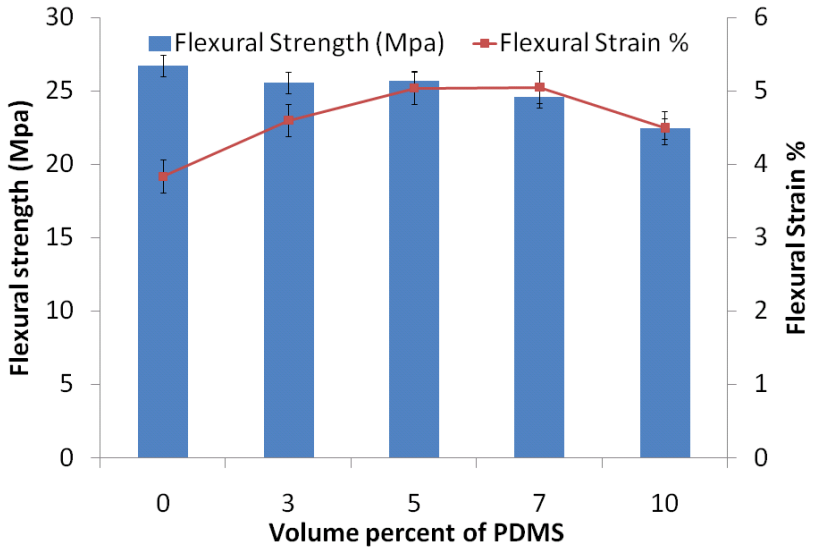

Fig3.6: Flexural Strength and Strain at Different PDMS vol%

3.4.2 Flexural Toughness

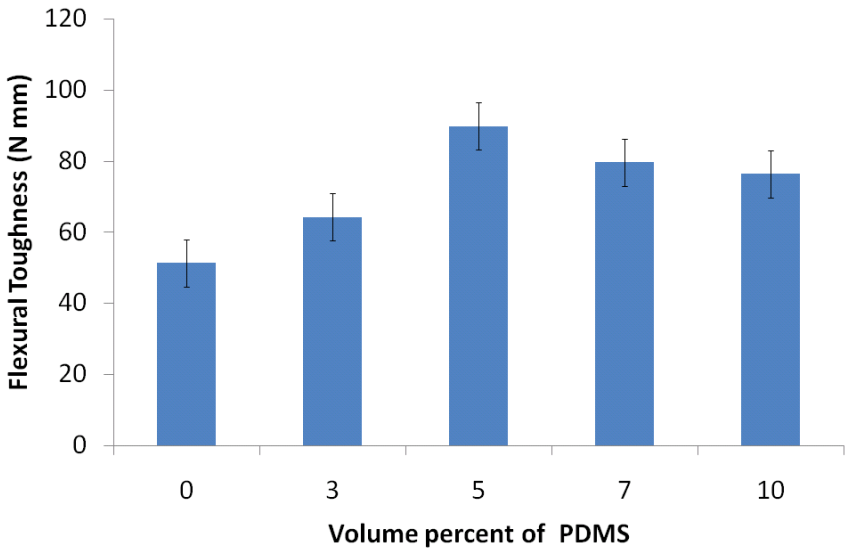

Fig3.7: Flexural Toughness of PDMS Syntactic Foams

3.5 Effect of PDMS Particle Size on Flexural Properties of Syntactic Foam

From the figure a. it is clear that PDMS loading at 5% gives optimum property, so selecting 5% as the PDMS content in syntactic foam, the behaviour of PDMS particle size on the flexural property is being studied. It is found that at varying particle size the flexural strength and strain is maximum in case of the particle size of 125-63µm. This is because of at finer particle size the problem of uniform distribution and coagulation of PDMS particle is occurred, by which properties of (125-63µm) lower PDMS particle size reinforced syntactic foams is decreased. Whereas larger particle results in reducing the interfacial area of PDMS

particle and matrix, which will results in lower flexural strength and toughness. PDMS particle that passes through the 125micron and retain by 63micron is the critical size range.

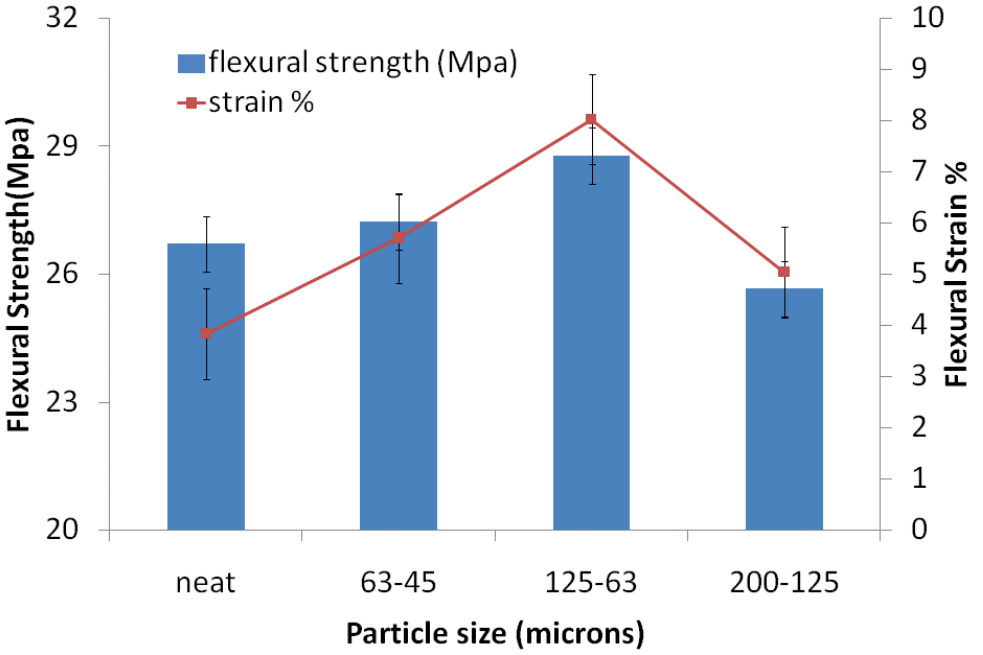

Fig3.8: Flexural Strength of PDMS loaded K15 Syntactic Foams

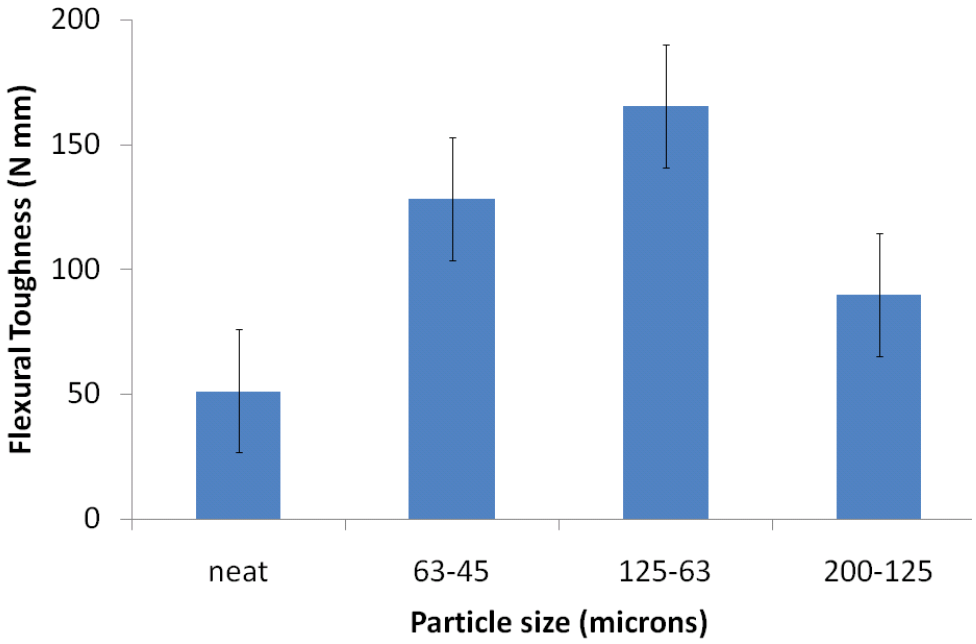

Fig3.9: Flexural Toughness of PDMS loaded K15 Syntactic Foams

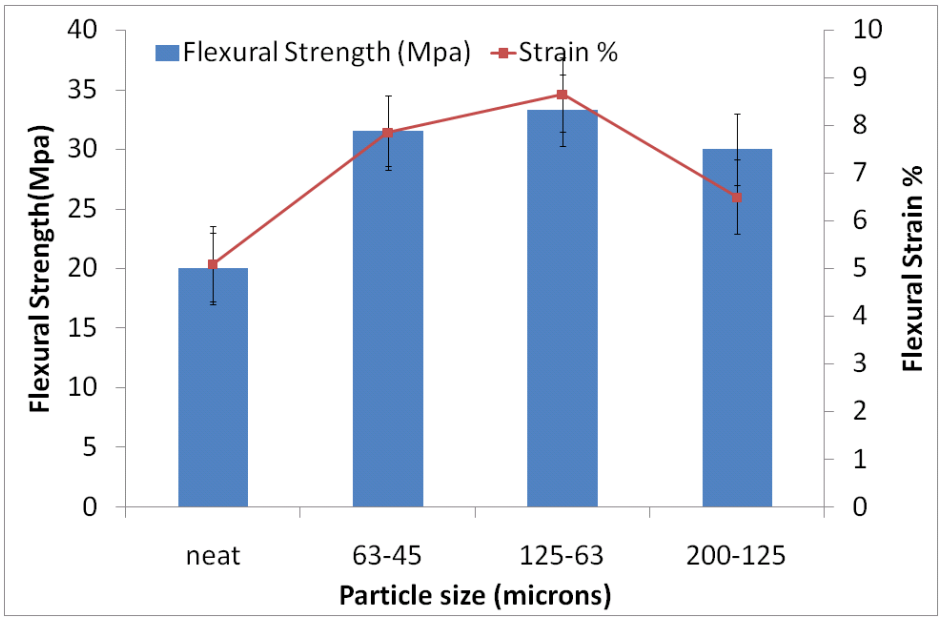

Fig3.10: Flexural Strength of PDMS loaded K46 Syntactic Foams

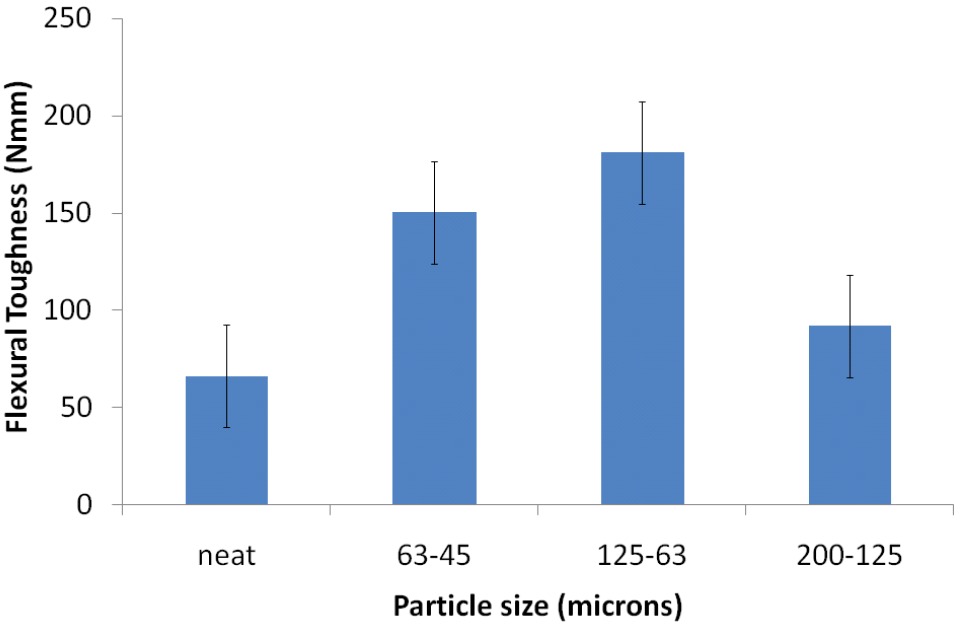

Fig3.11: Flexural Toughness of PDMS loaded K46 Syntactic Foams

3.6 Thermo Gravimetric Analysis

The TGA traces of epoxy syntactic foam in the presence of K46 HGM and toughened with PDMS microspheres at varying volume percentages is presented in figure 4. The figure shows a two step decomposition pattern in air atmosphere. A two stage degradation pattern can be seen in all the samples. The first step takes place at ~190 °C and is associated with the release of water and other condensable species. Char content increases on increasing the loading of PDMS microspheres and is maximum for 10 % (v/v) PDMS loading.

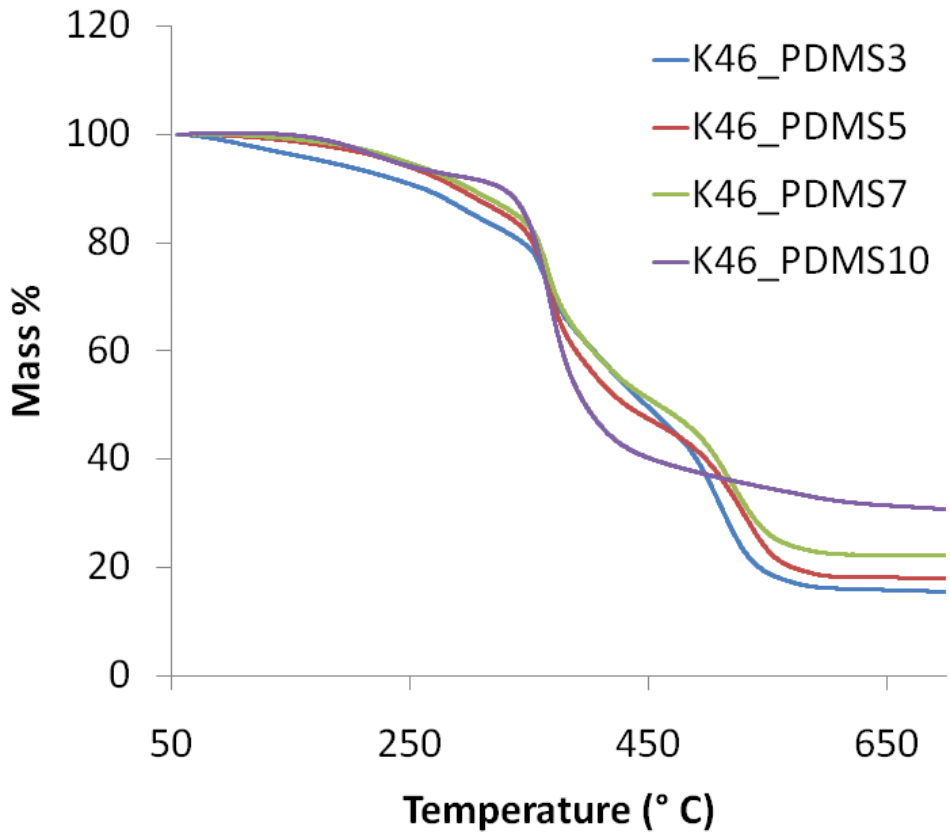

Fig 3.12: TGA of PDMS loaded Syntactic Foams

3.7 Scanning Electron Microscopy

The morphology of the silicone microspheres was carefully examined.

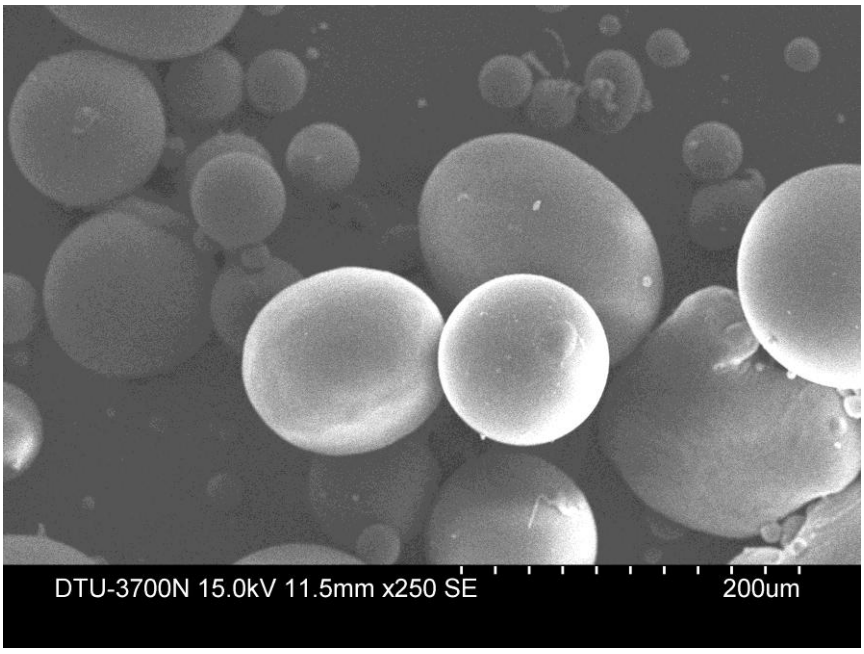

Fig 3.13:125µm Silicone Microsphere SEM Image

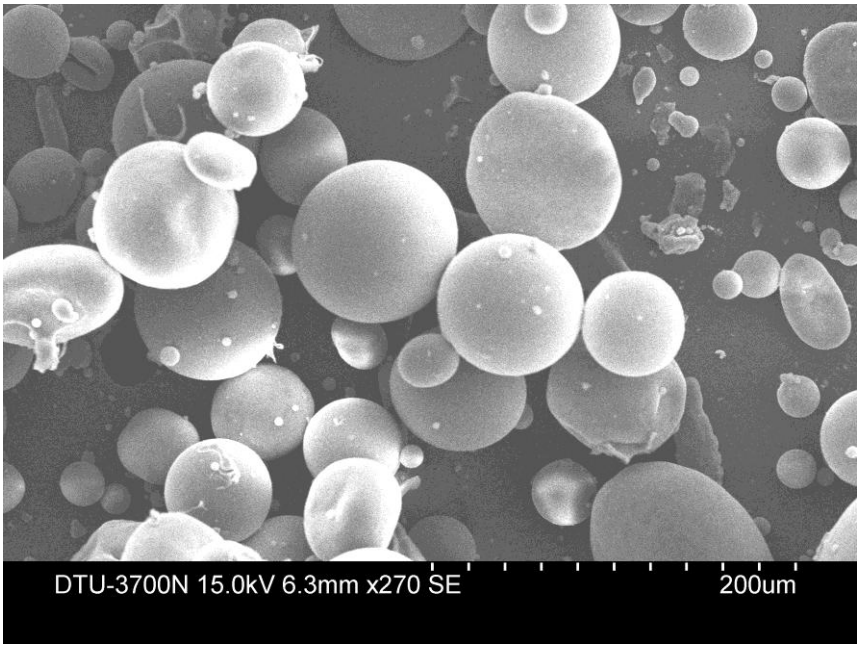

Fig 3.14:63µm Silicone Microsphere SEM Image

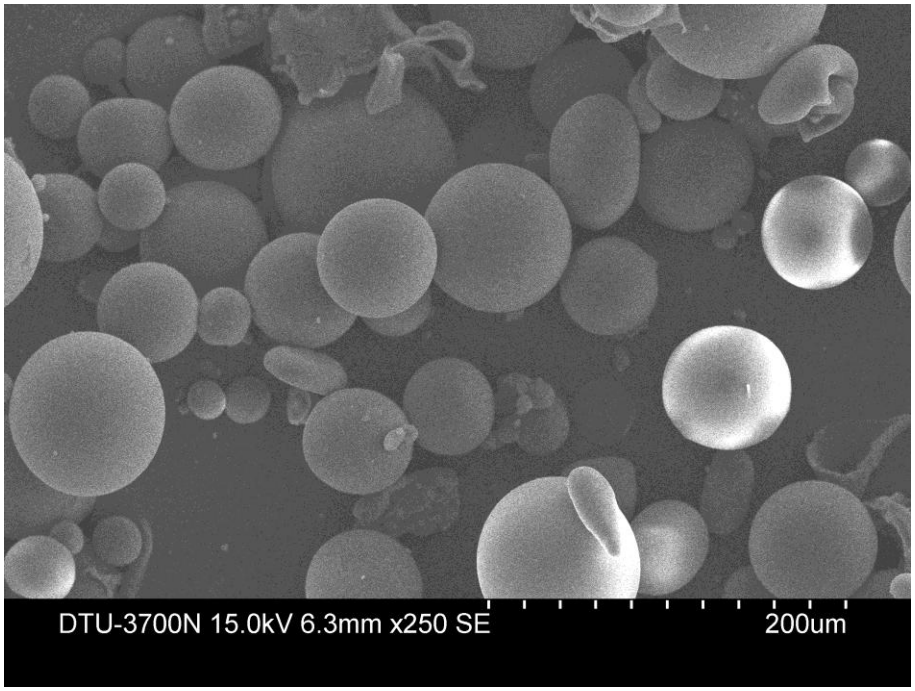

Fig 3.15:45µm Silicone Microsphere SEM Image

CHAPTER 4

SUMMARY AND CONCLUSION

Hollow particle filled polymers, more commonly known as 'syntactic foams' are lightweight materials with high damage tolerance. Syntactic foams are usually employed as core materials in sandwich composites. The use of such materials in aeronautical and space structures make it necessary to understand their characteristics under various environmental and loading conditions.

The present project deals with the development of syntactic foams consisting of hollow glass microballoons filled in epoxy matrix with a primary aim of reducing the density without compromising on the strength. As expected, syntactic foams were much lighter than epoxy, but the strength was also substantially lowered. Polydimethylsilicone (PDMS) microspheres were also included in the formulations to enhance the toughness of the base foam.

PDMS microspheres were synthesized by suspension polymerization process in suitable solvent. The operating parameters were optimized to obtain fine and uniform silicone microspheres. The microspheres were characterized by SEM imaging to determine their morphology.

Syntactic foams consisting of epoxy matrix and hollow glass microspheres of K15 and K46 (40-60 %v/v) were prepared. As commonly reported, some voids were also entrapped in the foams during their fabrication. The prepared foams were subjected to compression testing under quasi-static conditions (1.33 mm/min deformation rate). Under compression load, the entrapped microballoons ruptured and crushed leading to the absorption of energy till a certain limit after which abrupt increase in stress was observed that resulted in the failure of foams. Compression

strength was evaluated at different volume fractions of K15 and K46; the results indicating higher compression strength at lesser volume fractions of HGM i.e. at 40 percent. As expected, syntactic foams containing K46 microsphere exhibits higher strength and toughness as compared to K15 because of higher density.

Bigger size silicone microspheres (~200 µm) led to an increase in the strain percent at low volume percent of PDMS (up to 5%). But at high volume percent of PDMS (20%) flexural strength was much lower as strain percent decreased.

For relatively smaller size particles (~125µm) flexural strength decreases, but strain percent increases with increase in loading of PDMS as compared to neat syntactic foams. Maximum improvement in strain percent was observed at PDMS loading of 5 % v/v irrespective of the particle size (125 µm and 63 µm). Flexural strength and toughness of PDMS reinforced syntactic foams was much higher as compared to neat syntactic foam

CHAPTER 5

RECOMMENDATIONS FOR FUTURE WORK

Future activities which can be done in this field includes

- Preparation of syntactic foams exhibiting higher strength and low weight, good mechanical and chemical properties. For this purpose, other types of fillers can be investigated. Of particular interest is addition of nanofillers along with the microspheres.
- Along with silicone microspheres and glass microspheres, nanofillers such as nanoclay, nanofibers, graphene and CNT etc. can added and develop a new material for various applications.
- Another area of research is modelling and simulation of syntactic foam.

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