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Fracture toughness characterization of syntactic foams

Vijay Gorugantu

Louisiana State University and Agricultural and Mechanical College

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FRACTURE TOUGHNESS CHARACTERIZATION OF
SYNTACTIC FOAMS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Vijay Gorugantu
B.E., Andhra University College of Engineering, 1999
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ABSTRACT

Hollow particle filled polymeric materials called syntactic foams are used as core materials in sandwich composite structures. Syntactic foams find applications in aeronautical and space structures and therefore demand careful study and testing before they can be put to service. In the first part of this thesis work, syntactic foams are fabricated by varying the volume fraction of microballoons and also their density. Four different densities of microballoons are used ranging from 0.22 g/cc to 0.46 g/cc. The volume fraction of the microballoons is varied from 30% to 65%. A set of 3-point bending tests are conducted on these foam samples to determine their fracture toughness. It has been found that fracture toughness decreases with increase in volume fraction of the microballoons. As the microballoon density increases the fracture toughness also increases. From these current and previous studies it is found that the optimum volume fraction of microballoons is around 30%. Scanning Electron Microscopy analysis shows that at low volume fractions of 30% the failure mechanism is primarily due to the formation of micro cracks. These secondary micro cracks provide a toughening mechanism which is the reason for higher fracture toughness at this low volume fraction. As the volume fraction of microballoons increases due to the reduction in inter-particle distance, debonding occurs and the samples fail at much lower loads resulting in low fracture toughness values. In the second part of the study, samples are fabricated by incorporating two types of rubber particles. The volume fraction of the rubber particles is maintained constant at 2% and microballoon volume fraction at 63%. Load deflection curves show some limited plastic deformation just before the specimen fractures. Reinforcing with rubber increases the density by 15% and the fracture toughness by 35%. Rubber reinforcement also improves the crack propagation properties by changing the
fracture pattern to the ductile mode. There is strong adhesion between the rubber particles and the matrix material. Micrographs show the rubber particles fractured resulting in an increase of the fracture toughness.
CHAPTER 1
INTRODUCTION AND MOTIVATION OF THE RESEARCH

Modern day industrial applications demand materials with a specific set of properties. It is impossible for one particular type of material to have all the required properties from the wish-lists. This led to the development of composite materials obtained by the combination of two or more materials which have superior properties than its individual constituents. A formal definition of composite materials given by ASM hand book is “macroscopic combination of two or more distinct materials, having a recognizable interface between them” (ASM Handbook, 2003). Other definitions are “custom blending of materials with distinct characteristics lead to composites with tailor-made properties” (Composites, 2004b).

Some of the primary advantages of composite materials are high strength to weight ratio, high bending stiffness, corrosion resistance, excellent fatigue characteristics comparable to metals and good thermal insulation properties. The distinct advantage of composite materials is that the properties can be tailored according to the application requirements in the form of directional and spatial properties. Currently, the primary areas of application of composite materials are aerospace industry, automobile industry, ship building industry and sports equipment. The primary reason for this wide range of applications is the requirement of high strength to weight ratio for these industries.

Depending on the constituent materials, composites can be broadly classified into the following types:
1.1 Fiber Reinforced Composites

These are obtained by reinforcement of fibers in a matrix material. Reinforcing fibers can be made of metals, ceramics, glasses or polymers that have been turned into graphite and are known as carbon fibers. Fibers increase the modulus of the matrix material. This is because of the presence of strong covalent bonds along the length of the fibers. To break the fiber these covalent bonds are to be broken (Composites, 2004c). The property varies depending on the direction they are measured in. In general fibers have a very high modulus along their longitudinal axis, but have a very low modulus perpendicular (transverse) to their axis. Fiber reinforced composites are expensive to manufacture and are used in aerospace, sports equipment and race cars and generally not suitable for curved shaped components or structures.

1.2 Particulate Reinforced Composites

In this class of composite materials, fibers are substituted by particles in the matrix material. Particles used for reinforcing include ceramics and glasses, small mineral particles, metal particles such as aluminum and amorphous materials including polymers and carbon black. These particles help to increase the modulus of the matrix, decrease the permeability of the matrix and decrease the ductility of the matrix. These composites are less expensive when compared to fiber reinforced composites. An example of particle reinforced composites is an automobile tire which has carbon black particles in a matrix of polyisobutylene elastometric polymer (Composites, 2004a).

1.3 Sandwich Composite Structure

Among these class of materials is sandwich structured composites. These materials are popular due to their high specific strength and bending stiffness. Similar to
any other composite materials, these materials have significantly low density which makes them suitable for aeronautical, marine and space applications. These materials came into existence during the Second World War (Noor et al., 1996). A formal definition of these types of materials is: “A combination of different materials that are bonded to each other so as to utilize the properties of each separate component to the structural advantage of the whole assembly”. The properties of primary interest to look for in these materials are:

- High stiffness giving high flexural rigidity
- High tensile and compressive strength
- Impact resistance
- Surface finish
- Environmental resistance
- Wear resistance

A sandwich composite consists of three parts: two thin, stiff skins separated by a thick, light and a weaker core. The skins are bonded to the core by an adhesive to obtain load transfer between the components (Composites, 2004). This bond must be strong enough to resist the shear and tensile forces between them. The mechanical properties of sandwich composite structure depend on the skin, the core and the bonding between them. These properties could vary significantly depending on the assembly and manufacturing technique. Therefore, it is important to consider these in detail.

Skins are made up of two sheets of metal or similar materials which enclose the core. A wide variety of materials are used as skins which include sheets of aluminum, titanium, steel and fiber-reinforced composites. Special care needs to be taken
when selecting the skin because it comes in direct contact with the working environment. Depending on the application, the skin and the core can be of the same material or of different materials.

Cores used in load carrying sandwich constructions can be divided into four main groups; corrugated, honeycomb balsawood and foams. The most popular of these four types is the foams. This is because foams have low density and high strength. The core is mainly subjected to shear loading and the shear strain produces deformation and shear stresses. Therefore, core should be chosen in such a way that it will not fail under the application of shear load. The properties necessary for selecting a core are density, shear modulus, shear strength, stiffness perpendicular to the skins and thermal and acoustical insulation (Composites, 2004).

Some of the important areas of application of these sandwich composites are aerospace, packaging materials, marine applications, thermal and electrical insulation and in storage tanks, where a specific type of sandwich core material called syntactic foams are used.

1.4 Syntactic Foams: An Introduction

The core material in a sandwich composite structure as described above is subjected to transverse loading conditions. Therefore, careful selection needs to be made when selecting the core. Among the various materials available for cores, syntactic foams are one of the popular types. Others include metallic foams, ceramic foams, rubber foams etc. Syntactic foams are more popular because of their superior properties. These properties include:

- High strength/weight ratio
high bending stiffness
- easy fabrication procedure
- higher damage tolerance
- good vibration damping capacity

The word “syntactic” simply means that the foam is made by mixing microballoons (microspheres of borosilicate glass), ceramic spheres, or other lightweight aggregate within a resin system (Bunn & Mottram, 1993). These materials are known to be developed in the 1960’s as buoyancy materials for deep sea applications and are now being used in the marine and the aircraft industry (Malloy & Hudson, 1990 and Bardella & Genna, 2001).

Syntactic foams are fabricated by uniform dispersion of microspheres in a resin system. The filler material is the microsphere and the matrix material is the resin. This makes syntactic foams two phase structures. During fabrication some air is trapped within the matrix and is present in the form of voids in the final structure. This air rapped, acts as a third phase, making syntactic foams three phase structures. This can be seen in the following schematics (Figures 1.1 & 1.2) and SEM micrograph (Figure 1.3).

![Figure 1.1 Syntactic foam as a three phase structure](image)

**Figure 1.1 Syntactic foam as a three phase structure**
Figure 1.2 Syntactic foam as a three phase structure showing microballoons, matrix and voids

Figure 1.3 An SEM micrograph of a fracture surface at 40% volume fraction showing microballoons and voids within the resin matrix
Adequate research and testing needs to be done before these materials could be put to service. Accurate information on the compressive and facture properties is critical if these materials are to find more applications in the aerospace and marine industry. Many experiments have been conducted to determine the compressive properties of these materials. For their low density these materials exhibit good compressive load bearing characteristics.

A good understanding of fracture mechanics is needed for any material trying to find application in the aerospace industry. Not much work has been done in understanding the fracture mechanics aspects of syntactic foams. In an attempt to understand these aspects, experiments have been conducted to determine the fracture toughness characteristics of syntactic foams. Fracture toughness is defined as the resistance of a material to failure from fracture starting from a pre-existing crack. A set of 3-point bending tests have been performed on each type of syntactic foam specimens and micrographic analysis was conducted using scanning electron microscopy to understand the fracture pattern. Syntactic foams have been fabricated with rubber reinforcements and tests were conducted to determine whether there would be any change in the fracture pattern. Pure syntactic foams are known to fail in the brittle mode. Inclusion of rubber particles is known to change the fracture pattern to a ductile-brittle mode. Comparative analysis was done for syntactic foams with and without rubber reinforcements.

1.5 Scope of the Thesis

The initial part of the study, Chapter two starts with a critical review summarizing the earlier efforts made in trying to understand the mechanical properties of
these foams. Chapter three of the study identifies the key objectives based on the gaps in the past work. An experimental procedure is developed to test the fracture toughness properties of these foams. This is followed by the description of the raw materials used and fabrication techniques used in the fabrication of syntactic foams. All these are described in Chapter four. The results are presented and are discussed with the help of micrographs obtained from scanning electron microscopy in chapter five. The discussion is followed by conclusion in Chapter six and the references used in this work are listed in Chapter seven.

Several researches have developed innovative techniques to fabricate and test the mechanical and electrical properties of these foams. All those early efforts are summarized in the next chapter, Literature Review.
CHAPTER 2

LITERATURE REVIEW

Several efforts have been made in the recent past to develop new methods for fabrication of syntactic foams. Many literatures have been published on various aspects of syntactic foams and some of the relevant efforts are summarized here.

2.1 Studies on Fabrication

The three primary constituents in the fabrication of syntactic foams are (i) the matrix material (epoxy resin), (ii) the filler material and (iii) the curing agent to cure the matrix material. Some researchers use a fourth constituent, the diluent which helps in lowering the viscosity of the resin. Different types of resins have been tried in the past to fabricate syntactic foams. Bunn & Mottram (1993) used the cold-setting thermoset epoxy binder comprised of three components. Part one was “araldite” which is a mineral filled epoxy paste which increases the viscosity of the base resin and is an inexpensive way to increase the strength. The other two parts were also different forms of araldite used to enhance properties such as reduction in viscosity and curing time. The filler material used in these studies was phenolic microballoons. There have been studies on syntactic foams using polystyrene. In these, a small amount of polystyrene was mixed with glass bubbles and spread onto a fluoro-carbon coated pan that was exposed to 200°C for 2 minutes. This was done until the beads were fused. This beads mixture was mixed in an epoxy resin (Schott & Bhattacharjee, 1993). These foams exhibited mechanical properties similar to conventional foams.

Most of the studies used epoxy resin D.E.R-334 which is manufactured by Dow Chemical Company. This epoxy was hardened with a tetraethylene pentamine
curing agent and was diluted with a reactive diluent (Gupta et al., 2004 & D’Almeida, 1999). The other types of resins used in the fabrication process were modified epoxies, phenolics, polyurethanes, urethane acrylates and polyester and vinyl ester resins.

Several types of materials, hollow and solid were tried as filler materials. Depending on the properties required the filler material was selected. Most of the researchers used hollow glass microspheres (microballoons) made of borosilicate glass as the filler material (Gupta et al., 2004, Karthikeyan et al., 2000 and Kim & Oh, 2000). This filler material has been chosen as it has very low densities ranging from 0.22 g/cc to 0.5 g/cc. These microballoons have air trapped inside them which makes them lighter. Microballoons come in different diameters and are chosen depending on the strength desired. Metallic particles were used as filler materials when the strength requirement was high (Banhart, 2001). But it should be noted that using metallic particles as filler materials increases the weight of the syntactic foam. Wetzel & Haupert in 2003 used aluminum oxide and calcium silicate particles as filler materials. Azimi et al., (1996) fabricated syntactic foams by mixing different amounts of rubber and glass microballoons in a ductile epoxy polymer keeping the filler content constant. They found that the inclusion of rubber initiated a change in the crack propagation mechanism. Studies have been done on using industrial waste as reinforcement in epoxy composites. The filler material used in these studies was particulate powder obtained after drying the mud retained on the final sieving operation of a hydrometallurgical zinc plant. Using industrial wastes as filler materials saves the cost of their treatment and disposal (Rodelheimer & D’Almeida, 2001).
All of the above mentioned foams were made with different kind of resins and by using different filler materials. The general procedure followed by many is the resin diluted with the diluent to reduce viscosity. The hardener (curing agent) is later added stirring the mixture slowly. The microballoons used in most of the cases were hollow glass microballoons. This combination of epoxy resin binder and glass microballoons yielded desirable mechanical properties as discussed in the next section of this chapter.

2.2 Studies on Compressive Properties

As syntactic foams are light and brittle materials, compressive strength is of utmost importance. Many tests have been done and results published on the compressive characteristics of these foams. The first results on compressive strength were reported by Bunn & Mottram in 1993. They tested foams having volume fraction of microballoons between 0% and 53%. The maximum amount of microballoons in this case was 53% by volume. As the volume fraction of the microballoons decreased from 53% to 0% it was found that the bulk density increased from 0.78 g/cc to 1.5 g/cc. A linear relation was observed between the filler content and the bulk density. Compressive tests showed that the lowest strength was for foams having highest microballoon concentration. This indicates that the addition of microballoons reduced the compressive strength (Bunn & Mottram, 1993).

Palumo et al. (1996) have done compression tests at 15.38 wt% of microballoons. It was observed that the compressive strength reduced from 70 MPa to 50 MPa as the weight fraction of the microballoons increased from 15% to 35%. Micrographic analysis of the fracture surface indicated that the failure occurred due to
extensive debonding between the resin and the microballoons. SEM analysis also showed that some microballoons might have broken due to the mechanical mixing process when the foam was being fabricated. An analytical analysis was done and the experimental results were compared. The difference in strength was attributed to the mechanical damage of the microballoons which occurs in the course of composite preparation or may be due to residual thermal stresses around the glass sphere as a consequence of the inevitable mismatch between the coefficients of thermal expansion of the resin and the microballoons (Palumo et al., 1996).

D’Almedia (1999) studied the effect of changing the diameters of the glass microballoons on the mechanical properties. These studies showed that as the volume fraction of the microballoons increased, the mechanical properties decreased. The microballoons act as pores inside bulk resin matrix. At a fixed volume fraction, the compressive strength and elastic modulus are higher for composites fabricated with microballoons of smaller diameters (greater wall thickness). This means that smaller the microballoon, better the resistance to crack propagation. In other words, the use of microballoons with selected diameters permits one to maximize the use of these composites (D’Almedia, 1999).

Gupta et al. in 1999 worked on establishing a correlation between the raw materials processing route on one hand and void content on the other. The microballoon used in the fabrication process varied in the diameter range of 10-100 µm and the density was 0.25 g/cc. Compression tests and micrographic analysis was done. Calculations based on volumetric estimates showed that the void fraction was greater than 10%. This could be because of bubble formation and entrapment while the mixture was being stirred.
during fabrication. These bubbles form as voids in the final composite structure. The other reason for void formation was attributed to the incomplete wetting of the microballoons. During mixing, a film of resin might have enclosed a cluster of microballoons. This can happen when microballoons are of small size or when the viscosity of the resin is high. To avoid the formation of voids, authors tried using fibers along with microballoons and this reduced the void content to below 4%. Compressive tests performed showed that the compressive strength increased as the void content in the foam reduced from 10% to 4% (Gupta et al., 1999).

Studies on compressive failure features were done keeping the volume fraction constant at 67.8%. Shearing and wedge shaped crack appearance were observed in the compression test specimens. SEM micrographs showed the formation of debris which indicates that the specimens failed in a compressive mode (Gupta et al., 2001). Karthikeyan et al. (2000) studied the processing and compressive strengths of syntactic foams with and without fibrous reinforcements. They found that besides physical features like voids, microstructural variations do have a significant influence on the compressive behavior. The addition of fibers in low proportions of around 2% did not increase the compressive strength, whereas the addition of fibers in high proportions, around 6%, increased the compressive strength significantly. A microscopic analysis of the compressive fracture features revealed the following.

High magnification micrographs reveal the presence of plastic deformation marks that are in the form of steps. These marks cannot be generated if the matrix fractures in compression, but are possible in only shear type of failure. The presence of debris indicates that the samples failed in compression mode. These features
indicate the state of stress under loading. The banded structure appears due to the frequent change in the localized plane of crack propagation in a specific direction. Undamaged microballoons were seen all over the structure with a few broken fragments. In foams with fiber reinforcements, it was observed that there exists a preferred orientation of the fibers (Gupta et al., 2002).

Gupta et al. (2004) studied the effect of microballoon radii ratio and specimen aspect ratio (width/thickness) on the compressive properties. Radii ratio is the ratio of the inner diameter to the outer diameter of the microballoon. Changing radius ratio does not change any other parameters such as surface area of microballoon/matrix interfacial strength but changes the mechanical properties such as compressive strength and fracture properties. Compression tests showed that specimens tested in edgewise orientation have lower values of compressive modulus compared to that of flat wise specimen orientation because of lateral expansion.

Figure 2.1 Specimen orientation for (A) edge-wise loading and (B) flat-wise loading. Peak compressive strength in edgewise orientation showed dependence on crack propagation. Compression tests carried out with slabs of different radius ratio showed
that with decrease in radius ratio, the peak compressive strength and modulus increase. The strain at the peak compressive stress does not depend on the radius ratio and is a property that comes from the matrix resin (Gupta et al., 2004). Surface analysis after compressive testing indicated a sequential fracture pattern. Initially when compressive load is applied the microballoons in the top and bottom layers resist deformation and the load is transferred to the middle layer of microballoons. As more compressive load is applied the weakest microballoon in the middle layer fractures forming a void and debris. This results in neighboring microballoons being damaged due to load transfer from the weakest microballoon. This slowly results in the whole of middle layer being crushed. This phenomenon of crushing transfers towards the top and bottom of the compressive test specimen and finally it fails. This mechanism of compressive fracture was framed from the microscopic studies of the fractured specimen. This phenomenon is termed as layered crushing. This occurs in the case of high density foams. The low density foams fail by a phenomenon called longitudinal splitting which occurs in the following sequence (Kim & Plubrai, 2004).

- Formation of 3-6 longitudinal cracks along the compression specimen
- Widening of these longitudinal cracks, and
- Failure at one end of the specimen resulting in further lateral expansion.

Very little work has been published on the fatigue properties of syntactic foams. One published work is by Azimi et al. (1996) on the ways to improve poor crack propagation. Two approaches for achieving this are: (i) Modification of epoxy matrix using compliant rubbery particles, and (ii) Reinforcement of epoxy polymers using rigid
inorganic fillers or thermoplastic particles. This study states that addition of particles beyond a critical volume fraction does not result in significant improvement in toughness of foams. To further enhance crack resistance, hybrid epoxy composites (epoxy with rigid glass particles and compliant rubber particles) have been used. The amount of rubber and glass particles was varied keeping their volume fraction constant. These slabs when tested showed an improvement in the fatigue crack propagation rate. The second phase particle interactions induced a transition in fatigue crack propagation behavior of rubber modified polymer. When the size of the plastic zone at the crack tip becomes large compared to the size of rubber particles crack shielding mechanism becomes more active. The presence of rubber particles in the vicinity of hollow particles suppresses the micro-cracking mechanism of microballoons by relieving the triaxial tension (Azimi at al., 1996).

Studies by Kim & Oh (2000) on the impact behavior of syntactic foams states that inclusion of hollow glass microballoons in resin reduces the impact force/stress. Compression tests conducted showed that the modulus of the foam reduced by a factor of two from that of the pure resin. A scanning electron micrograph of the fractured compression test specimen showed broken microballoons. The broken specimens showed that the failure mode is by shear on planes inclined approximately 45° to the loading direction. Kim & Khamis (2001) have done experiments to determine the fracture characteristics by varying the volume fraction of the microballoons. The specific flexural strength decreased as the volume fraction of microballoons increased. The specific fracture toughness decreased with increase in the volume fraction of the microballoons. SEM analysis showed that microballoons on the top surface crushed. This
was observed for specimens having volume fraction of 65%. The composites with high volume fractions of microballoons tend to lose matrix fracture characteristics because of being dominated by microballoons. Experiments on impact tests demonstrated that addition of microballoons from 0% to 65% volume fraction decreased the impact force three times. It was concluded that impact performance of these composites as protective materials can be enhanced by increasing the microballoon content, but this can be achieved at the expense of other mechanical properties (Kim & Khamis, 2001).

2.3 Studies on Fracture Properties

Benderly et al. (2004) studied the effect of changing the resin and curing agent on the fracture toughness and flexural strength of syntactic foams. This study had the following findings:

- Fracture toughness of syntactic foams can be improved by changing the resin and curing agent without sacrificing the mechanical, thermal properties or density.

- The fracture toughness of anhydride based syntactic foams can be improved by addition of elastomer.

- The foam composition determines the failure mechanism. This change in failure mechanism with the foam type is the reason for the increase in fracture toughness of certain foams.

- Using cycloamine curing agent rather than anhydride curing agent yielded a 30% increase in fracture toughness due to better curing properties.
• In the case of cycloamine curing agent the failure mechanism is different from that of anhydride curing agent and the crack propagates through the matrix. This might be the reason for their high fracture toughness.

Zihlif & Ragosta (2001) studied the yielding and fracture toughness characteristics of syntactic foams. They reported that the density, elastic modulus, compressive yield stress and strain decreased with increase in the volume fraction of microballoons. The fracture toughness and the fracture energy did not vary significantly with change in temperature in the range of 50 to 125°C. The fracture surface of unfilled epoxy (0% volume fraction of microballoons) showed some features of primary cracks near the notch which was introduced prior to the testing. The secondary cracks appeared as parabolic striation marks. These marks imply that plastic deformation and shear yielding accompany the fracture process. Once the volume fraction of microballoons is increased from 30% to 60%, these markings tend to disappear.

An interesting study done by Wouterson et al. in 2004 compared to the above studies states that the fracture toughness of syntactic foams increased as the volume fraction of the microballoons increased. This study was done by using two different types of microballoons. The volume fraction of microballoons varied from 0% to 20%. For the fracture toughness tests the aspect ratio, a/W ratio (crack length/specimen width) was chosen to be 0.5. The following formula was used to calculate the fracture toughness.

\[ K_{IC} = Y \frac{3PS\sqrt{a}}{2BW^2} \]  

(2.1)

Where, Y is the geometric configuration factor in polynomial terms and is expressed as:
\[ Y = 1.93 - 3.07 \left( \frac{a}{W} \right) + 14.53 \left( \frac{a}{W} \right)^2 - 25.11 \left( \frac{a}{W} \right)^3 + 25.80 \left( \frac{a}{W} \right)^4 \]

\[ P = \text{peak load at the onset of crack growth in a linear elastic facture} \]

\[ W = \text{width of the specimen} \]

\[ S = \text{support span, and} \]

\[ a = \text{crack length in a single edge notched specimen} \]

Figure 2.2 Schematic of the specimen showing dimensions

After accessing the fracture toughness the linear elastic energy release rate was calculated using the equation:

\[ G_{ic} = \frac{K_{ic}}{E} \left( 1 - \vartheta^2 \right) \quad (2.2) \]

Where,

\[ \vartheta \] is the Poisson ratio, and

\[ E \] is the Elastic Modulus = \[ \frac{S^3 m}{4bd^4} \]
Where,

\[ b = \text{width} \]
\[ d = \text{depth} \]
\[ S = \text{span length, and} \]
\[ m = \text{slope of the tangent to the initial straight line portion of load-deflection curve.} \]

It was stated that the linear trend observed would reach an optimum value with increasing filler content. It was suggested that the maximum filler content arose due to an increasing inter-particle separation and an increase in the number of microspheres that can be debonded from the matrix. The microcracks formed by the debonding ahead of the crack tip will facilitate crack propagation and reduce the facture toughness as microballoons content increases further.

The observed increase in the facture toughness with increasing volume fraction of microballoons is attributed to crack front bowing mechanisms which assumes that the microspheres can resist crack propagation and cause crack front to bow out between the microspheres. Results from this study show that the high density microballoons contribute to higher strength and stiffness in addition to crack bowing mechanisms. The enhancement of facture toughness in this case can be attributed to higher strength of the filler content. Tests to determine the impact resistance showed that the impact resistance decreased with the increase in volume fraction of microballoons (Wouterson et al., 2004).

Recently, there have been limited studies focusing on the development of nano-composites with superior properties such as tribological and optical properties.
Addition of alumina nano-particles into epoxy resin improves stiffness, impact energy and failure strength at low filler contents of 1%. There is also an improvement of wear resistance at 2% volume fraction of alumina particles. Introduction of calcium silicate particles in the nano-composite increases the flexural bending modulus and the wear resistance. Both nano-particles and micro-particles increase wear resistance, but the underlying mechanism is different (Wetzel et al., 2003). Ding & Merk (1997) studied the improvement of wear and adherence properties of syntactic foam coatings by gradually increasing the volume fraction. They found that this increase leads to an optimization of wear resistance and adherence to the substrate of electrodeposited composite coatings.

2.4 Other Properties

Studies on hygrothermal effects (environment and temperature) on damage tolerance of composite sandwich panels have been done at the NASA/Marshall Space Flight Center, Huntsville, Alabama. These studies state that the moisture absorption was higher for syntactic foams than the skins of the sandwich composites structure. Strength of the syntactic foam reduces significantly with moisture absorption (Hodge et al., 2000).

Several studies have been conducted in assessing the optical properties, dielectric properties and temperature dependence of electrical properties of epoxy composites (Ramadin et al., 1996 & Shahin et al., 1996 & Shahin et al., 1995). These studies show that impedance in general increases with the increase in volume fraction of microballoons and the dielectric constant decreases with both frequency and filler content.
2.5 Studies on the Applications of Syntactic Foams

There are several instances in the literature which mention the areas of specific application of syntactic foams. The Navy needs materials which can meet the following properties.

- Broader performance capabilities
- Improved lethality
- Increased survivability
- Longer life expectancy, and
- Reduced life cycle costs

“Fire performance” tests have been done which state that syntactic foams pass almost all the fire performance tests except the ignitability and the burn-through test. It was suggested that the variation in the composition might result in syntactic foam passing all the tests (Tessier, 2001).

Material characterization for composite nose cap of a solid rocket booster was done at NASA/Marshall Space Flight Center, Huntsville, Alabama. The nose cap needs structural integrity and protection from aerodynamic heating. The tests show that syntactic foam could meet the design requirements after brief exposure to high temperature (Hodge et al., 2000).

Studies on application of syntactic foams as insulation equipment in any subsea environment were done at the Cuming Corporation. Results show that syntactic foams could sustain the high temperature and pressure if careful choice is made while selecting the resin and the filler material (Wang & Watkins, 2002).
2.6 Analytical and Numerical Studies

Mechanics of open and closed cell foams have been studied by Sanders & Gibson (2002). Their study was conducted using finite element models of simple cubic hollow spheres. These studies show that closed cell foams have significantly higher mechanical properties when compared to open cell foams. Rizzi et al. (2000) studied the mechanical properties of syntactic foams by doing experiments and verifying the results with the models created. They followed an engineering mechanics approach and the bi-modulus modified Drucker-Prager model which has been calibrated from the bi-axial tests conducted. They concluded that their models completely agreed with the experimental findings (Rizzi et al., 2000).

Leggoe et al. in 1998 followed a two-scale modeling approach to simulate the deformation behavior of syntactic foams. They tested foams of volume fraction range between 0% to 40%. It was concluded that as property distributions became less uniform, the range of strain developed in the three dimensional arrays increases. Yield stress and the strain hardening increased as the severity of clustering increased. Even the elastic modulus increased with clustering. Bardella & Genna (2001) studied the elastic behavior of syntactic foams. Their finding was that the change in the wall thickness of the microballoons used had a very little effect on the mechanical behavior of the foams. The second most important aspect is that the presence of unwanted voids which accumulate during the fabrication of syntactic foams have a significant effect on the elastic modulii of the composite.

Summarizing all the above stated studies it can be said that a lot of literature has been published in the area of syntactic foams but all these studies have been
done using different matrix and filler materials. This makes it very complicated to compare the results for validity. As the areas of applications of syntactic foams are primarily in the aeronautical sector careful research needs to be done before they can be used as structural members. A detailed study needs to be done on all the mechanical properties using the same raw materials. This will help us in comparing and validating the results.

Much of the literature published is on the compressive fracture features of syntactic foams. As syntactic foams are used as core materials in sandwich composite structures, compressive strength is of utmost importance. Apart from good compressive characteristics syntactic foams also have good damage tolerance characteristics. Therefore adequate knowledge is to be gained in understanding the fracture behavior of these materials. A few of the published works studied the fracture toughness characteristics, but none of them to my knowledge provide a complete understanding of the fracture toughness characteristics. These aspects need to be understood before syntactic foams can be put to application.

This thesis focuses on characterizing fracture toughness with the variation in several other parameters. These parameters are the volume fraction of the filler material and their density. Micrographic analysis is also conducted to better understand the failure behavior of these materials. Based on a critical review of the available literature it was found necessary that understanding the aforesaid aspects of fracture mechanics will add a new dimension to the application of syntactic foams. The key objectives have been identified and are mentioned in the next chapter, Chapter three, Research Objectives.
CHAPTER 3

RESEARCH OBJECTIVE

The objective of the present research is to develop an understanding of the fabrication processes and fracture toughness aspects of closed cell syntactic foams. The values of fracture toughness can be obtained by conducting the 3-point bend tests of syntactic foam specimens. From these values of fracture toughness one can predict the behavior of structures with pre-existing cracks.

In the previous section on Literature Review, major work done in this area has been summarized. Several properties have been evaluated and various fabrication techniques have been developed, but the researchers used different resins, curing agents and filler materials. Therefore, it is difficult to compare the results obtained because different resins and fillers have different properties. Therefore, a standardized fabrication technique needs to be developed using the same raw materials and mechanical properties need to be evaluated, so that their comparison would provide better insight into the understanding of fabrication, testing and applications of syntactic foams.

The second most important aspect to note is that several authors published results on the variation of mechanical properties with variation in microballoon volume fraction. There are only a very few instances where different densities of microballoons have been used along with the variation in volume fraction. At this juncture it can be concluded that the mechanical properties of syntactic foams can be varied in the following two possible ways.

- The first method is to change the volume fractions of the matrix and microballoons in the composite structure.
• The second method is to use microballoons of different internal radius but the same external radius keeping the same volume fractions of the matrix resin and the microballoons. Changes in different internal radii mean that microballoons have different wall thickness.

Mechanical properties have been evaluated either using the first or the second method. It would be interesting to look at the variation in certain mechanical properties by conducting experiments varying the volume fraction of the microballoons as well as varying the densities of microballoons. These are the parameters used in the calculation for the density of the composite.

A major proportion of the experimental work on mechanical properties of syntactic foams focused on compression properties. Good compressive properties are desired due to specific applications of syntactic foams in aerospace and marine structures. This is evident from the previous chapter. It should be noted that syntactic foams have yet another very important property of good damage tolerance. Not much work has been done in evaluating the fracture behavior aspects of syntactic foams. It would be interesting to look at the fracture toughness aspects to study its variation by varying the volume fraction of microballoons and their density. Based on the above discussion, the objectives of this study are summarized below.

3.1 Objectives of the Study

This study is primarily divided into two parts. The first part deals with the fracture toughness tests and micrographic analysis of pure syntactic foams. The second part of the study deals with the behavior of syntactic foams fabricated with rubber reinforcements. The second part also compares the fracture toughness results of syntactic foams with and without rubber reinforcements. A detailed description of the key research objectives identified is given below:
3.1.1 Pure Syntactic Foams

1) Fabricate syntactic foams with varying volume fraction
2) Test these syntactic foams for their fracture toughness using 3-point bending equipment.
3) Derive a relationship between the fracture toughness and microballoon volume fraction and microballoon density. At each volume fraction syntactic foam slabs were fabricated using four different microballoon densities and tested.
4) Conduct micrographic analysis of the fractured surfaces using the Scanning Electron Microscope.
5) Compare the results of this study with the results available in the literature.

3.1.2 Syntactic Foams with Rubber Reinforcements

1) Fabricate syntactic foams with the incorporation of rubber reinforcements of volume fraction 2% and microballoons volume fraction of 63%. This volume fraction is chosen as it is the maximum fraction at which complete dispersion of the microballoons within the matrix material can be obtained within the matrix (Gupta, 2003). Above this value the volume fraction of voids increase and cannot be controlled.
2) Two types of rubber particles are to be used.
3) To compare the results of (a) pure syntactic foams having microballoon volume fraction of 65% to (b) syntactic foams with rubber reinforcements (63% microballoon volume fraction and 2% rubber reinforcement volume fraction).
Based on the above objectives an experimental program has been
devised which includes the fabrication and testing procedures carried out to determine
the fracture toughness values. All these aspects are discussed in the next chapter,
Chapter 4, Experimental Program.
CHAPTER 4

EXPERIMENTAL PROGRAM

Syntactic Foams can be fabricated with varying compositions by changing either the raw materials used for fabrication or the composition of raw materials used. The common raw materials used in the fabrication of syntactic foams are:

- The resin which is the matrix material,
- A curing agent to cure the matrix material,
- A diluent which helps in reducing the viscosity of the resin, and
- The microballoons which is the filler material.

In this present study the same set of raw materials have been used in fabricating all the foam slabs, but their compositions have been varied to study the changes in facture properties. The details of the raw materials used and why they have been selected compared to their counterparts has been explained in detail, in the following sections.

Raw Materials used for fabrication of syntactic foams:

4.1 Matrix Resin

The matrix resin is the core material in the syntactic foam. It adds strength and structural integrity to the syntactic foam structure. Among the commercially available epoxy resins D.E.R 332 a di-epoxy resin manufactured by the DOW chemical company is selected for this study. The advantages this epoxy resin offers over other epoxies, as stated by the manufacturer, are maximum epoxide equivalent weight of 178 (chemically pure diglycidyl ether of bisphenol-A would have an epoxide equivalent weight of 170), high purity, lack of polymer fractions, low viscosity and improved
properties at elevated temperatures, (Epoxide equivalent weight is the weight of resin in grams which contains one gram equivalent of epoxy. The lower the epoxide equivalent weight, the better for syntactic foams). The commercially available epoxies that have been considered for this application are given in the Table below. The most suitable candidate is the D.E.R-332. The epoxy D.E.R-337 has a lower viscosity but is not the better choice because of its high epoxide equivalent weight. Its high epoxide equivalent weight increases the weight of the syntactic foam structure which is not desirable. The better choice would be the D.E.R-332 which has the optimum epoxide equivalent weight and viscosity. The low viscosity helps in uniform wetting of the filler material. The chemical name of this resin 2,2-bis [4-(2’3’ epoxy propoxy) phenyl] propane. This resin is popularly called as diglycidyl ether of bisphenol A(DGEBA) (Dow Plastics, 2004a). The superior properties of this resin when compared to other similar resins for this application are shown in the Table 4.1 below.

Table 4.1 Typical properties of some Liquid Epoxy Resins

<table>
<thead>
<tr>
<th>Resin Name</th>
<th>Epoxide Equiv. Wt.</th>
<th>Viscosity Range (cps@25°C)</th>
<th>Specific Gravity 25/25°C</th>
<th>Weight (Lbs/Gal) @25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.E.R-317</td>
<td>192-203</td>
<td>16000-25000</td>
<td>1.16</td>
<td>9.7</td>
</tr>
<tr>
<td>D.E.R-330</td>
<td>176-185</td>
<td>7000-10000</td>
<td>1.16</td>
<td>9.7</td>
</tr>
<tr>
<td>D.E.R-331</td>
<td>182-192</td>
<td>11000-14000</td>
<td>1.16</td>
<td>9.7</td>
</tr>
<tr>
<td><strong>D.E.R-332</strong></td>
<td><strong>172-176</strong></td>
<td><strong>4000-6000</strong></td>
<td><strong>1.16</strong></td>
<td><strong>9.7</strong></td>
</tr>
<tr>
<td>D.E.R-337</td>
<td>230-250</td>
<td>400-800</td>
<td>1.16</td>
<td>9.7</td>
</tr>
<tr>
<td>D.E.R-362</td>
<td>185-205</td>
<td>4500-6500</td>
<td>1.14</td>
<td>9.5</td>
</tr>
<tr>
<td>D.E.R-364</td>
<td>190-210</td>
<td>4000-7000</td>
<td>1.16</td>
<td>9.7</td>
</tr>
<tr>
<td>D.E.R-383</td>
<td>176-183</td>
<td>9000-10500</td>
<td>1.16</td>
<td>9.7</td>
</tr>
</tbody>
</table>
The chemical formula of this resin is presented in the following Figure (Figure 4.1).

![Chemical formula of the resin D.E.R 332 used as the matrix material](image1)

**Figure 4.1 Chemical formula of the resin D.E.R 332 used as the matrix material**

To further reduce the viscosity of the resin which ensures uniform wetting of the filler material, the diluent is added. The properties of the diluent used for fabrication are discussed below.

### 4.2 Diluent

Large volume fraction of the microballoons can be mixed uniformly in the resin if the viscosity of the resin is low. Hence, a diluent is added to lower the viscosity of the resin matrix. Adding diluent C₁₀-C₁₄ aliphatic glycidyl ether, commercially known as ERISYS-GE 8 in 5% by weight quantity brings down the viscosity of the resin from about 4 N.s.m⁻² at 20°C to about 2 N.s.m⁻². This diluent is being supplied by CVC Specialty Chemicals. The data sheets and the technical information provided by the manufacturer states that addition up to 5% by weight of this diluent increases the tensile strength and the modulus of the epoxy resins. Average equivalent epoxide weight of the diluent is in the range of 275-300. The weight per gallon at 25°C in kilograms is 3.36 and the specific gravity is 0.9 (CVC Specialty Chemicals Inc, 2004). The chemical formula of the diluent is shown below (Figure 4.2).

![Chemical formula of Aliphatic Glycidyl Ether (Diluent)](image2)
The hardener or the curing agent which cures the epoxy after the fabrication process is discussed next.

4.3 Hardener

Hardener is a curing agent added to the matrix to harden the resin mix. Triethylene tetramine (TETA), a polyfunctional aliphatic amine, is used as a curing agent. This Chemical is commercially known as D.E.H. 24 and is manufactured by DOW Chemical Company. The chemical formula of TETA is \( \text{C}_n\text{H}_{18}\text{N}_4 \). The amines react with the epoxy group through the active amine hydrogen. Molecular weight of this hardener is 146.4 and weight per active hydrogen is 24.4. Aliphatic amine based hardeners cure at room temperature, provide excellent chemical and solvent resistance to the polymer solutions and retain physical properties in the long term. The curing time is very low i.e. it cures with epoxy resins within 30 minutes (Dow Plastics, 2004). The chemical formula of the hardener is as shown below.

\[
\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2
\]

Figure 4.3 Chemical formula of Hardener (TETA) molecule (Dow Plastics, 2004)

The filler materials added to lower the density of the syntactic foam structure are discussed below.

4.4 Microballoons

These are hollow glass microspheres that are alternatives to conventional fillers and additives such as silicas, calcium carbonate, talc, clay etc., for many demanding applications. These low density particles are used in a wide range of industries to part weight, lower costs and enhance product properties. These bubbles are
manufactured through a multi-step process in which glass is formed at high temperature from soda lime borosilicate, milled to fine particle size, and then run through a high temperature heat transfer process. These glass bubbles have low viscosity, high filler loading and reduced weight.

Four types of borosilicate glass microballoons are used for the fabrication of syntactic foam specimens. The commercial names of these four types are S-22, S-32, S-38 and K-46. The number they are represented by indicates the density of the microballoons (For instance the S-22 has a density of .22 g/cc). The properties of these microballoons are detailed in the following Table (Table 4.2). The microballoon size distribution indicates the number of microballoons having the particular size. The tenth percentile indicates that 10% of particles are in the given size distribution range (Microballoons Selection Guide, 2004). The average true particle density indicates the density of the microballoons and the pressure for minimum 80% fractional survival indicates the pressure 80% of the microballoons can sustain without breaking. These microballoons were manufactured and supplied by 3M Company under the trade name “Scotchlite”. Distribution of outer diameter of the microballoons is approximately same, but the inner diameter varies. The microballoon wall thickness can be related to a parameter called radius ratio $\eta$.

$$\eta = \frac{r_i}{r_o} \quad (4.1)$$

Where $r_i$ and $r_o$ are the internal and external radii of the microballoons.
Increase in $\eta$ corresponds to a decrease in wall thickness, which leads to a decrease in true particle density of the microballoon. Therefore, microballoons having higher values of $\eta$ give rise to lower particle syntactic foams and vice versa.

Table 4.2 Properties of microballoons (Microballoons Selection Guide, 2004)

<table>
<thead>
<tr>
<th>Microballoon Type</th>
<th>Microballoon Size Distribution ($\mu$m)</th>
<th>Average True Particle Density (kg/m$^3$)</th>
<th>Pressure for Min. 80% Fractional Survival (MPa)</th>
<th>Radius Ratio $\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10$^{\text{th}}$ percentile</td>
<td>50$^{\text{th}}$ percentile</td>
<td>90$^{\text{th}}$ percentile</td>
<td></td>
</tr>
<tr>
<td>S-22</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>S-32</td>
<td>20</td>
<td>40</td>
<td>75</td>
<td>320</td>
</tr>
<tr>
<td>S-38</td>
<td>15</td>
<td>40</td>
<td>75</td>
<td>380</td>
</tr>
<tr>
<td>K-46</td>
<td>15</td>
<td>40</td>
<td>70</td>
<td>460</td>
</tr>
</tbody>
</table>

4.5 Rubber Particles

Rubber reinforcements generally add strength to the syntactic foam structure. Some of the syntactic foam slabs have been fabricated using rubber reinforcements to check for the variation in strength. These rubber particles are solid particles procured from Rouse Polymers. The details provided by the manufacturer are given in the Table below (Table 4.3). The numbers in the trade name indicate the mesh sizes of the rubber particles.
Table 4.3 Properties of rubber particles

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Particle Size (microns)</th>
<th>Specific Gravity Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF-80</td>
<td>75</td>
<td>1.12-1.15</td>
</tr>
<tr>
<td>GF-170</td>
<td>40</td>
<td>1.12-1.15</td>
</tr>
</tbody>
</table>

4.6 Mold

The mold consists of two stainless steel plates having dimensions of 229 mm x 229 mm x 13 mm. It consists of a top and bottom plates and a frame in between. The picture below (Figure 4.5) shows the arrangement of the mold. The frame is fixed to the bottom plate with bolts and after the foam is spread uniformly on the bottom plate until it comes to the height of the frame, the upper plate is fixed with the help of wing nuts. The plates and the frame are made of stainless steel as it resists corrosion and is strong to resist bending when the upper plate is tightened.

![Mold setup used for fabricating syntactic foams](image)

It should be made sure that the fabricated syntactic foam does not stick to the surface of the mold plates. To ensure this a mold release agent is applied to the surfaces of the plates before fabrication.
4.7 Mold Release Agent

Dow Corning-111 Sealant and Lubricant is used as a release agent in the molds. This sealant is a silicone based white translucent gel. Selection of this release agent is based on a service temperature range of -57°C to 204°C. This lubricant is moisture resistant and resistant to oxidation. The specific gravity of this release agent is 1.0 (Dow Corning, 2004).

Using all the above raw materials syntactic foams are fabricated by following the procedure given below.

4.8 Fabrication Procedure

1. As a first step the stainless steel mold is taped on its side and surfaces with scotch tape and Dow Corning 111 mold release agent is applied on both the surfaces. Taping is done in two layers to ensure that the stainless steel surface is fully covered and there are no gaps in between. When fabricating syntactic foams with low volume fractions care was taken to ensure that an ultra thin layer of mold release agent separates the plates and the foam.

2. Next, the resin (D.E.R-332) and diluent (C10-C14) are mixed (in the ratio of 19:1) together and heated to 50°C to reduce the viscosity (the viscosity reduces from 4 N.s.m$^{-2}$ to 2 N.s.m$^{-2}$ when 5wt% of the diluent is added). This is done in order to ensure uniform mixing and complete wetting of the microballoons. To ensure that the viscosity of the resin is sufficiently lowered it is mixed with the diluent in the ratio of 19:1 (Gupta, 2003). The calculations are shown the Tables (Table 4.5 & 4.6) below.

3. Next, depending on the volume fraction of the microballoons, the microballoons are weighed; for this study the volume fraction varies from 30% to 65%).
4. Next, 13.74 parts of hardener are mixed with 100 parts of the resin diluent mixture and the mixture is uniformly stirred. These values have been obtained by using formulae involving the epoxide equivalent weight (Gupta, 2003).

5. The weighed microballoons are added slowly with continuous stirring of the mixture. Uniform mixing is ensured by using a mechanical stirrer. Care was taken not to damage the microballoons while stirring. It was made sure that bubbles formed during stirring should be allowed to degas. These bubbles if not removed will form as voids in the final syntactic foam structure and will result in a reduction of strength. As syntactic foams are fabricated manually void fraction below 10% is acceptable and the fabricated slabs had a void fraction below this range.

6. After sufficient stirring for 15 minutes, the mixture was cast in the stainless steel mold. The dough was spread uniformly in the mold. After the dough was spread uniformly in the mold the upper plate of the mold was tightened. Next the cast slab was allowed to cure for 36 hours at room temperature and then cured for 3 hours at 150°C in the oven. This is considered as the optimum cure time for the epoxy and the curing agent used. All the syntactic foam slabs are fabricated in the same procedure and the Table 4.4 gives the list of various syntactic foam slabs fabricated.

7. For syntactic foams with rubber reinforcements, the same procedure described above is followed. The rubber particles are added along with the microballoons. Uniform stirring was ensured so that no gas bubbles will form in the final syntactic foam structure. But, in syntactic foams, with high volume fractions of microballoons, gas bubbles were trapped during fabrication and were present in the form of voids in the final structure. The void fraction varied from 2% to 10% depending on the volume fraction of the microballoons.
mixed. At low volume fraction of microballoons the void fraction was very low (in the order of 2%) whereas at high volume fractions of 65% and in the rubber reinforced slabs the void fraction was around 10%.

Fabrication of syntactic foams with 30% volume fraction of microballoons was complicated as the mixture had very low viscosity. Due to this very low viscosity, the air gap between the bottom plate and the frame was a source of leak. To stop the leaking of the sample from the air gap the junction area was taped. The upper plate was not fixed when fabricating syntactic foam slabs with 30% microballoon volume fraction. Fabrication of syntactic foam slabs with 40% and 50% volume fraction of microballoons was easy as the viscosity of the mixed dough was just right to be poured into the mold. When fabricating foams with 60% microballoon volume fraction and above, it was found difficult to ensure uniform mixing of microballoons. This was evident in the calculations of the void fraction in the syntactic foam slabs.

Table 4.4 List of syntactic foam slabs fabricated

<table>
<thead>
<tr>
<th>Volume Fraction of Microballoons</th>
<th>Density of Microballoons</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>40%</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>50%</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>60%</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>65%</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>65% with Rubber particles of size 45µm</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
<tr>
<td>65% with Rubber particles of size 75µm</td>
<td>S-22, S-32, S-38, K-46</td>
</tr>
</tbody>
</table>
Table 4.5 Calculations of proportions of raw materials in fabrication of syntactic foams-1

<table>
<thead>
<tr>
<th>Particle Volume Fraction</th>
<th>Particle Volume</th>
<th>Particle weight</th>
<th>Total Resin</th>
<th>Resin</th>
<th>Diluent</th>
<th>Hardener</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>84</td>
<td>18.48</td>
<td>756</td>
<td>609.7707</td>
<td>41.83575</td>
<td>104.3936</td>
</tr>
<tr>
<td>20</td>
<td>168</td>
<td>36.96</td>
<td>672</td>
<td>542.0184</td>
<td>37.18734</td>
<td>92.79434</td>
</tr>
<tr>
<td>30</td>
<td>252</td>
<td>55.44</td>
<td>588</td>
<td>474.2661</td>
<td>32.53892</td>
<td>81.19505</td>
</tr>
<tr>
<td>40</td>
<td>336</td>
<td>73.92</td>
<td>504</td>
<td>406.5138</td>
<td>27.8905</td>
<td>69.59576</td>
</tr>
<tr>
<td>50</td>
<td>420</td>
<td>92.4</td>
<td>420</td>
<td>338.7615</td>
<td>23.24208</td>
<td>57.99646</td>
</tr>
<tr>
<td>60</td>
<td>504</td>
<td>110.88</td>
<td>336</td>
<td>271.0092</td>
<td>18.59367</td>
<td>46.39717</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle Volume Fraction</th>
<th>Particle Volume</th>
<th>Particle weight</th>
<th>Total Resin</th>
<th>Resin</th>
<th>Diluent</th>
<th>Hardener</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>84</td>
<td>26.88</td>
<td>756</td>
<td>609.7707</td>
<td>41.83575</td>
<td>104.3936</td>
</tr>
<tr>
<td>20</td>
<td>168</td>
<td>53.76</td>
<td>672</td>
<td>542.0184</td>
<td>37.18734</td>
<td>92.79434</td>
</tr>
<tr>
<td>30</td>
<td>252</td>
<td>80.64</td>
<td>588</td>
<td>474.2661</td>
<td>32.53892</td>
<td>81.19505</td>
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<td>336</td>
<td>107.52</td>
<td>504</td>
<td>406.5138</td>
<td>27.8905</td>
<td>69.59576</td>
</tr>
<tr>
<td>50</td>
<td>420</td>
<td>134.4</td>
<td>420</td>
<td>338.7615</td>
<td>23.24208</td>
<td>57.99646</td>
</tr>
<tr>
<td>60</td>
<td>504</td>
<td>161.28</td>
<td>336</td>
<td>271.0092</td>
<td>18.59367</td>
<td>46.39717</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle Volume Fraction</th>
<th>Particle Volume</th>
<th>Particle weight</th>
<th>Total Resin</th>
<th>Resin</th>
<th>Diluent</th>
<th>Hardener</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>84</td>
<td>31.92</td>
<td>756</td>
<td>609.7707</td>
<td>41.83575</td>
<td>104.3936</td>
</tr>
<tr>
<td>20</td>
<td>168</td>
<td>63.84</td>
<td>672</td>
<td>542.0184</td>
<td>37.18734</td>
<td>92.79434</td>
</tr>
<tr>
<td>30</td>
<td>252</td>
<td>95.76</td>
<td>588</td>
<td>474.2661</td>
<td>32.53892</td>
<td>81.19505</td>
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<td>406.5138</td>
<td>27.8905</td>
<td>69.59576</td>
</tr>
<tr>
<td>50</td>
<td>420</td>
<td>159.6</td>
<td>420</td>
<td>338.7615</td>
<td>23.24208</td>
<td>57.99646</td>
</tr>
<tr>
<td>60</td>
<td>504</td>
<td>191.52</td>
<td>336</td>
<td>271.0092</td>
<td>18.59367</td>
<td>46.39717</td>
</tr>
</tbody>
</table>
Once the syntactic foam slabs were fabricated, they have been cut to the required dimensions for testing using the cutting saw wheel. The cutting and specimen preparation procedure adopted is described below.

### 4.9 Specimen Cutting and Preparation for Testing

- Specimens of dimensions 60 mm x 12 mm x 6.3 mm are cut using the cutting wheel. These dimensions have been chosen for this study to compare the results with previous work.
Figure 4.6 Cutting machine used to cut the syntactic foam samples

- Once the specimens have been cut, care was taken in marking and identifying them, as all the specimens look alike. Once cut, they were polished on a fine grit sand paper (No 350) to remove the epoxy rich surface layer. Syntactic foams are generally epoxy rich on the surface.

- After polishing the length and weight of the samples was noted. These values will be used in the density calculations later.

- The samples were marked for their span length of 50-mm, leaving 5-mm on either side for supports. The center of the specimen was also marked for load application.
• Once these dimensions are marked, the dimensions of the specimens, the width and the thickness were noted. The thickness and the width were taken at three different points and an average of these values was used in the calculation of density and fracture toughness.

• An a/W (crack length to the specimen width) ratio of 0.5 was selected for testing the fracture toughness. This value was taken from previous available literature.

• The notch was made using a vertical band saw (accuracy 0.1mm) and all the specimens were notched.

![Vertical band saw used to introduce notch in the 3-point bend specimen](image)

**Figure 4.7** Vertical band saw used to introduce notch in the 3-point bend specimen
• The notch was sharpened to a fresh crack using a razor blade. The razor blade was placed in the notch and tapped 3 times to ensure that a fresh crack is formed. The notch created and the freshened crack together was equal to half the width of the specimen.

Once these steps have been completed the specimens were ready for the three point bend test which is described in the next section.

4.10 3-Point Bend Testing Apparatus

MTS machine at the Southern University Facility was used to perform the three point bending test to determine the fracture toughness. A three pint bend fixture was used along with the MTS machine. An upper grip and a lower grip were manufactured at the workshop to fit the 3 point bend fixture into the grips of the MTS machine. The single-edge notched bend specimens were loaded in three point bend geometry. The load was applied at the center of the specimen and the two supports were placed at either ends of the specimen where the span length markings have been made. The MTS machine had a data logger which provided the load displacement data from which the peak load to the onset of crack growth was taken. The MTS machine also provides the stress strain data but only the load displacement data was taken. The maximum load of the load cell used was 150kN. The upper limit for the load was set to be 200N as it was noted from all previous studies that syntactic foam samples would fracture much before this load. The crosshead speed was chosen to be 0.5mm/min. The following pictures show the MTS machine used and its data logger. The specimen in place for testing is also shown in Figures 4.8 and 4.9.
Figure 4.8 MTS machine used for testing 3-point bend specimens

Figure 4.9 Experimental set up showing the specimen in place
4.11 Fracture Toughness Calculation

Fracture Toughness was calculated according to Wouterson et al. (2004) to compare the results obtained. The same specimen dimensions, a/W ratio and span length were used. The difference is that this study incorporated four different types of microballoons and volume fractions of microballoons from 30% to 65%. Wouterson et al. used two densities of microballoons and varied the volume fraction from 0% to 20%. There was one density of microballoon common to both the studies and its results could be used for comparison. The stress intensity factor, $K_{IC}$ can be estimated from the following equation (Wouterson et al., 2004).

$$K_{IC} = Y \frac{3PS\sqrt{a}}{2BW^2}$$

(4.2)

Where, Y is a Geometric Factor which can be calculated from

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.80\left(\frac{a}{W}\right)^4$$

Where,

P = the peak load at the onset of crack growth in a linear elastic fracture

W = is the width of the specimen,

B = is the thickness of the specimen,

S = the support span, and

a = the crack length

The a/W ratio of all the samples was maintained around 0.5. The width and thickness were the averages of three readings taken along the length of the specimen. The peak load was taken from the load displacement data generated and the calculations for fracture toughness were done by using Microsoft excel.
4.12 Preparation for Scanning Electron Microscopy

After the samples fractured sections of the fractured surface were cut using a vertical band saw. One section was cut from each of S-22 and K-46 microballoons. These two densities of microballoons were chosen for SEM analysis because of the density difference that exists between them. These sections were cut for all volume fractions ranging from 30% to 65%. The sections were cut and then stuck on to the mount using rubber cement. Later, they were allowed to dry for 24 hours until the cement hardened. The samples were then coated with a sputter of gold coating which makes them conductive to be seen in the scanning electron microscope. The picture taken after the samples were gold coated is in Figure 4.10. After coating scanning electron microscopy was done to observe the fracture surface of the syntactic foam specimens.

![Fracture Surface](image)

**Figure 4.10 Gold coated fracture surfaces for SEM**

The fracture toughness results obtained are discussed in the next chapter, Chapter five, Results and Discussion.
CHAPTER 5
RESULTS AND DISCUSSION

Syntactic foams were fabricated using the procedure described in the previous chapter, Chapter 4. The measurement of density of the fabricated slabs yielded the following results.

5.1 Density Measurement for Pure Syntactic Foams

The fabricated syntactic foam slabs were measured for their density. This was done by dividing the mass of the syntactic foam sample by the volume of the sample. The weight and dimensions of the samples cut for the 3-point bend test were taken. The values of calculated density with the variation in volume fraction for four different types of microballoons are shown in the Table 5.1.

Table 5.1 Calculated densities of fabricated syntactic foam slabs

<table>
<thead>
<tr>
<th>Volume Fraction of microballoons</th>
<th>Density S-22(g/cm³)</th>
<th>Density S-32(g/cm³)</th>
<th>Density S-38(g/cm³)</th>
<th>Density K-46(g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>0.8232</td>
<td>0.8668</td>
<td>0.8705</td>
<td>0.9032</td>
</tr>
<tr>
<td>40%</td>
<td>0.7455</td>
<td>0.7962</td>
<td>0.8057</td>
<td>0.8265</td>
</tr>
<tr>
<td>50%</td>
<td>0.6156</td>
<td>0.6668</td>
<td>0.6888</td>
<td>0.7322</td>
</tr>
<tr>
<td>60%</td>
<td>0.5358</td>
<td>0.5932</td>
<td>0.6136</td>
<td>0.6538</td>
</tr>
</tbody>
</table>

It can be seen from the Table that as the volume fraction of the microballoons increases the density decreases. This can be observed for all four different densities of microballoons. The increase in microballoon density from S-22 to K-46 increases the density of the fabricated foam slab. This is due to the additional weight of the microballoons having higher wall thickness. As can be seen from Table 5.1 that at 60%
volume fraction of microballoons the density increases by 15% when the microballoon density increases from 0.22 g/cc to 0.46 g/cc. The variation of density of the fabricated foam slab with variation of volume fraction is shown in Figure 5.1 below. The variation is shown for four different densities of microballoons. It can be seen that as the density of the microballoooon increases the density of the fabricated foam slab also increases. It should be noted here that this increase in density results in an increase in the fracture strength.

![Figure 5.1 Variation of density of fabricated slabs with variation in volume fraction and density of microballoons](image)

5.2 Density Measurement for Syntactic Foams with Rubber Reinforcements

Density measurements have been made on syntactic foams fabricated with rubber reinforcements. The fabricated foam slabs have 63% volume fraction of microballoons and 2% volume fraction of rubber particles. The density values have been calculated in the same way as described in the case of pure syntactic foams shown in
section 5.1. Dimensions have been recorded for all the four different densities of microballoons. The sizes of the rubber particles are 45µm and 75µm. The variation of the density of fabricated slabs with variation in density of microballoons for the two types of rubber particles used is shown below (Figure 5.2).

![Graph showing variation of density with microballoon density](image)

**Figure 5.2 Variation of density with variation in microballoon density for two types of rubber particles**

It can be noted from the Figure 5.2 that as the microballoon density increases the density of the fabricated syntactic foam slab increases. In general the density should increase as the size of the rubber particles increases but the recorded values show that the density of the slab fabricated with smaller rubber particles shows higher density values at microballoon densities of 0.22 g/cc and 0.46 g/cc. This is due the difference in the volume fraction of the voids in the fabricated foam slabs. At higher volume fractions of 65% as the microballoon content increases it becomes difficult to achieve complete wetting of the microballoons. A group of microballoons form as a cluster and the air gaps in between them are trapped as voids. This is the reason for the inconsistent slab densities observed at microballoon densities of 0.22 g/cc ad 0.46 g/cc.
The plot below (Figure 5.3) shows the comparison of density of syntactic foams with and without rubber reinforcements. Comparison of 60% volume fraction with 63% microballoon volume fraction and 2% rubber particles shows that as rubber particles are introduced into the syntactic foam the density and the weight increase. The 60% curve and the rubber particles curve converge at microballoon density of 0.38 g/cc. This can be attributed to the difference in volume fraction of voids in the fabricated syntactic foam slab. This ambiguity can be resolved by considering more number of data points in to determine the true behavior. The lines appear to converge at 0.38 g/cc density of microballoons due to the variation in the volume fraction of the voids in the syntactic foam structure. Therefore, for designing syntactic foam structures it should be kept in mind that rubber reinforcements do increase the strength but at the cost of increase in weight.

Figure 5.3 Comparison of syntactic foams with 60% microballoon volume fraction with foams having 63% microballoons and 2% rubber particles
Rubber particles are generally added to sandwich composite structures to improve the crack propagation and damping properties.

5.3 Fracture Toughness of Pure Syntactic Foams

Four different densities of syntactic foams were tested for varying volume fractions of 30%, 40%, 50%, 60% and 65%. The load displacement curves were plotted using Microsoft Excel. Six specimens were tested for each type of syntactic foam and load displacement curves of three specimens have been plotted. It was found that the peak load and the behavior of the foam is consistent in at least five of the six specimens tested. The load displacement curves of the syntactic foams tested at all volume fractions are shown in the following pages. The discussion on load displacement curves is presented later in this section. These curves are presented in the order of increasing volume fraction of microballoons (Figures 5.4 to 5.23). In all these Figures the specimen numbers are indicated by Sp.

![Load Displacement curve of syntactic foam having 30% volume fraction of microballoons and density of 0.22g/cc](image)
Figure 5.5 Load Displacement curve of syntactic foam having 30% volume fraction of microballoons and density of 0.32g/cc

Figure 5.6 Load Displacement curve of syntactic foam having 30% volume fraction of microballoons and density of 0.38g/cc
Figure 5.7 Load Displacement curve of syntactic foam having 30\% volume fraction of microballoons and density of 0.46g/cc

Figure 5.8 Load Displacement curve of syntactic foam having 40\% volume fraction of microballoons and density of 0.22g/cc
Figure 5.9 Load Displacement curve of syntactic foam having 40% volume fraction of microballoons and density of 0.32g/cc

Figure 5.10 Load Displacement curve of syntactic foam having 40% volume fraction of microballoons and density of 0.38g/cc
Figure 5.11 Load Displacement curve of syntactic foam having 40% volume fraction of microballoons and density of 0.46g/cc

Figure 5.12 Load Displacement curve of syntactic foam having 50% volume fraction of microballoons and density of 0.22g/cc
Figure 5.13 Load Displacement curve of syntactic foam having 50% volume fraction of microballoons and density of 0.32g/cc

Figure 5.14 Load Displacement curve of syntactic foam having 50% volume fraction of microballoons and density of 0.38g/cc
Figure 5.15 Load Displacement curve of syntactic foam having 50% volume fraction of microballoons and density of 0.46g/cc

Figure 5.16 Load Displacement curve of syntactic foam having 60% volume fraction of microballoons and density of 0.22g/cc
Figure 5.17 Load Displacement curve of syntactic foam having 60% volume fraction of microballoons and density of 0.32g/cc

Figure 5.18 Load Displacement curve of syntactic foam having 60% volume fraction of microballoons and density of 0.38g/cc
Figure 5.19 Load Displacement curve of syntactic foam having 60% volume fraction of microballoons and density of 0.46g/cc

Figure 5.20 Load Displacement curve of syntactic foam having 65% volume fraction of microballoons and density of 0.22g/cc
Figure 5.21 Load Displacement curve of syntactic foam having 65% volume fraction of microballoons and density of 0.32g/cc

Figure 5.22 Load Displacement curve of syntactic foam having 65% volume fraction of microballoons and density of 0.38g/cc
Figure 5.23 Load Displacement curve of syntactic foam having 65% volume fraction of microballoons and density of 0.46g/cc

All the load deflection curves (Figures 5.4 to 5.23) show that the syntactic foam behaves like a linear elastic brittle material without significant plastic deformation. This is evident from the negligible plastic deformation before the specimen fractures. It is evident that for almost all the specimens at low volume fractions the failure is very sudden (Figures 5.4 to 5.12). An experimental observation is that at low volume fractions of 30% and 40% the specimen fractured more in a brittle mode. The brittle fracture is quite evident from the steep drop in the load as can be observed from Figures 5.18 to 5.22. As the volume fraction of the microballoons in the syntactic foams increased (60% & 65%) the load deflection curve dropped gradually as can be seen in Figures 5.18 to 5.23. It can be noticed from these Figures that there is limited plastic deformation in the latter part of the loading curve. This indicates that the fracture is more brittle at low
volume fractions. In some tests the load increased and fell suddenly and then increased again. This can be seen in Figures 5.8, 5.11 and 5.13. This could be due to the air voids trapped in the syntactic foam during fabrication. These voids are trapped air bubbles during fabrication. When load is applied and a void is encountered in the crack path there is a drop in load due to fast crack propagation and when the propagating crack encounters the foam material the load increases steadily. This could also be attributed to the crush of a group of microballoons present as a cluster in the syntactic foam. The first reason seems to be more valid after observation of the micrographs.

Studies undertaken by Wouterson et al. (2004) also show that the load deflection curve drops suddenly. This is because they tested syntactic foams with low volume fractions (0% to 20%). At higher volume fractions the load deflection curve is in a more zigzag fashion (Figures 5.18 to 5.23). This is due to the higher volume fraction of microballoons present in the syntactic foam. Every time a microballoon got crushed there was a drop in load and then an increase. There was no change in the slope of the load deflection curve as the microballoon density increased at each volume fraction. For example this can be observed in Figures 5.4 to 5.7 for volume fraction of 30%. The only change was that there is an increase in the peak load as the microballoon density increased. As the volume fraction of microballoons increased it was observed that the peak load dropped indicating a decrease in strength.

To access the fracture toughness, 3-point bend tests were conducted on the syntactic foam samples. The values of fracture toughness were calculated from equations 4.2. At all volume fractions of microballoons it can be observed from the
Figure below (Figure 5.24) that the fracture toughness increased with increase in the density of microballoons.

![Figure 5.24 Variation of Fracture Toughness with variation in Density of Microballoons](image)

The increase in fracture toughness was observed to be uniform at all volume fractions except for the increase in toughness from 65% to 60%. As the volume fraction of the microballoons increased from 60% to 65% the plot (Figure 5.24) shows that the fracture toughness decreases more than 30%. This decrease is higher than the decrease of fracture toughness at lower volume fractions. This is because the maximum packing fraction of microballoons within the matrix is around 65% and as the volume fraction approaches close to this value there is reduction in compressive strength (Gupta, 2003). The highest recorded value of fracture toughness was 2 MPa.m$^{0.5}$ and this was recorded for microballoon volume fraction of 30% and density 0.46 g/cc. As the volume
fraction increased from 30% to 65% the fracture toughness decreased from 2 MPa.m^{0.5} to 0.6 MPa.m^{0.5} indicating that an increase in the filler content reduces strength. Studies conducted by Wouterson et al. (2004) show that as the filler content increases, the fracture toughness increases. They tested volume fractions in the range of 0% to 20% whereas in this thesis work, tests have been performed for volume fractions in the range of 30% to 65%. This shows that there might exist an optimum volume fraction of microballoons at which the fracture toughness goes to a maximum. This is discussed later in this chapter. As the volume fraction of the microballoons increased from 30% to 65% the decrease in fracture toughness is uniform.

Figure 5.25 Variation of fracture toughness for each microballoon type with variation in volume fraction
When the fracture toughness data is plotted for each microballoon density with variation in volume fraction of microballoons the trend (Figure 5.25) shows that as the volume fraction increases the density decreases and this happens for all densities of microballoons tested. The key thing to note here is that the variation in volume fraction from 30% to 65% has a more significant effect when compared to variation in density of microballoons from 0.22 g/cc to 0.46 g/cc. When the volume fraction increases from 60% to 65% the decrease in fracture toughness is 30%. This is because 63% is considered the maximum volume fraction of microballoons and an increase above this induces higher volume fraction of voids in the matrix. During design of structural components to achieve a wider range of properties like compressive strength and fracture toughness, changing the volume fraction of microballoons would be advantageous than changing the microballoon density. Figure 5.25 shows that there is a uniform trend of the fracture toughness dropping with increase in volume fraction of microballoons.

Comparing Figures 5.24 and 5.25, it is evident that changing the volume fraction of the microballoons from 30% to 65% has an impact of three times more on the fracture toughness than by changing the density of the microballoons from 0.22 g/cc to 0.46 g/cc. Similar trends were obtained by Wouterson et al. in 2004 when the K-15 and K-46 densities of microballoons were compared for volume fractions ranging between 0% to 20%. The effect of changing the volume fraction from 0% to 20% resulted in a 30% increase in the fracture toughness whereas the increase in density of microballoons from 0.15 g/cc to 0.46 g/cc increased the fracture toughness by only 10%. This indicates that increasing the wall thickness of the microballoons increases the fracture toughness.
properties but is not as significant when compared to the effect of changing the volume fraction.

Comparison of results obtained in this study with studies conducted by Wouterson et al. (2004) show that there exists an optimum value of microballoon content at which the fracture toughness goes to a maximum value. They studied the variation of fracture toughness of K-15 and K-46 types of microballoons. The volume fraction varied from 0% (pure resin) microballoons to 20%. Similar trend was observed for both densities of microballoons. A comparison of their study with the present study is shown in Figure 5.26 below.

![Figure 5.26 Variation of fracture toughness with microballoon volume fraction, comparison of present study with study done by Wouterson et al. in 2004](image)

In the above plot (Figure 5.26) the two studies are compared. The fracture toughness might reach a peak value in-between volume fraction of 20% to 30% and after 30% the fracture toughness drops indicating that filler content reduced the strength. This region is represented as the extrapolated regime in the Figure. It can be seen that at some point
between 25% and 30% the fracture toughness might go to a peak value. It was stated that a similar trend would also be observed in the case of composites with glass beads having densities in the range of 2.5 g/cc. In more than half of the experiments performed it was observed that the optimum value of the filler content was between 20% and 30% (Lee & Yee, 2000). It was observed here that the fracture toughness of these composites reaches a maximum value at optimum content of glass beads. The reason for this is explained in the next section with the aid of micrographic analysis.

5.4 Micrographic Analysis

Micrographic analysis was done using Scanning Electron Microscopy to study the fracture surfaces. The fractured surface was sectioned using a vertical band saw. The surfaces were coated with a gold sputter and were studied for their fracture features. Syntactic foams with S-22 (Density 0.22 g/cc) and K-46 (Density 0.46 g/cc) microballoons were studied. These densities were chosen as any difference in fracture features will be evident because of the density difference that exists between them. One sectioned fractured surface was taken for each type of microballoon density at all volume fractions. The fracture surface of a three point bend specimen can be divided into three distinct regions: pre-crack, process zone and fast fracture zone (Lee & Yee, 2000). The pre-crack zone is produced by the razor blade wedging open the crack. The process zone is the tensile zone where the crack propagates first due to the applied load. The fast fracture region is the compressive region where the final fast fracture occurs.

The region of primary interest is immediately next to the crack initiation phase which is the process zone. The second most important region is the fast fracture region. This region is the compressive region. The crack after it reaches this zone leads to
fast final fracture. The SEM study was conducted in two zones for each specimen. The first one is the compressive zone and the second being the tensile zone. The top few layers of the specimen in the vicinity of the pre-introduced crack is the tension zone. This zone undergoes tension when the load is applied. The bottom layers are subjected to compression when load is applied and this region is called the compression zone. These zones of interest are as shown in Figure 5.27.

![Figure 5.27 Schematic showing the compressive and tensile zones in a 3-point bend specimen](image)

When the load is applied first the crack propagates through tension and then the final fracture occurs when the crack propagates to the compressive zone. A detailed study has been done in both these zones of interest.

At 30% volume fraction of microballoons the fracture features are more representative in the tensile region. Micro cracking phenomenon can be seen in the SEM micrograph shown in Figures 5.28 and 5.29. There is crack formation in both the tensile and compressive regions. The cracks can be seen more predominantly in the tensile region (Figure 5.28B). The lower magnification micrograph of the tensile region shows micro cracks propagating. These micro cracks are in the form of tail like structures which
can be seen in Figure 5.28. The higher magnification photograph (Figure 5.29) of the tensile region shows micro crack formation in the matrix material. As can be seen in Figure 5.29 the failure is due to the micro crack propagation mechanism and a scan of the fracture surface while conducting SEM analysis revealed that a few of the microballoons were broken.

Figure 5.28 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 30% volume fraction, S-22 Microballoons

Figure 5.29 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 30% volume fraction, S-22 Microballoons
Series of these micro cracks result in the formation of steps in the fracture pattern (Figure 5.29B). The series of step formation is because of two secondary crack fronts separated by a glass microballoon meeting each other. Lee and Yee (2000) report the same phenomenon while conducting studies with glass beads. These lines and steps seen in Figures 5.28 & 5.29 are formed when crack fronts are arrested for a certain period of time and break away upon further loading. This is typical at low microballoon volume fraction of 30%. At higher volume fractions the mechanism changes and is described in the next few sections.

![Figure 5.30 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 30% volume fraction, K-46 Microballoons](image)

**Figure 5.30 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 30% volume fraction, K-46 Microballoons**

In the case of foam slabs fabricated with K-46 microballoons it can be seen in Figures 5.30 and 5.31 that the failure mechanism is also due to micro crack propagation. Tail like features can be seen in Figure 5.30A and these are the micro cracks. These micro cracks meet and hinder the propagation of the primary crack. These cracks are going around the microballoons indicating that microballoons are resisting
deformation though some of the microballoons directly in the path of the primary crack have been deformed (Figure 5.31B).

Figure 5.31 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 30% volume fraction, K-46 Microballoons

Several cracks can be seen in the Figures 5.28 to 5.31 that are at 30% volume fraction, the cracks are more predominant in the tensile region. This is because after the initial crack is introduced with the razor blade, with the application of load the crack propagates through the tensile region. The reason for low percentage of micro cracks in the compressive region is that once the crack propagates through the tensile region there is a fast fracture in one direction. Debonding of the matrix material around the microballoons occurs but is negligible. Debonding is the failure of the interface between the matrix and the microballoons.

Compared to the micrographs at 30% volume fraction the micro cracks in the case of 40% volume fraction have reduced but they can be seen in the high resolution SEM micrographs (Figure 5.33). The tensile region has a comparatively more number of
micro cracks than the compressive region as can be seen from Figure 5.33 B and A respectively.

Figure 5.32 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 40% volume fraction, S-22 Microballoons

Figure 5.33 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 40% volume fraction, S-22 Microballoons
Another interesting observation here is that there are more number of microballoons crushed in the compressive region than in the tensile region (Figure 5.33). This is evident in both densities of microballoons S-22 and K-46. Overall observation of the fracture surface showed the same trend.

Figure 5.34 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 40% volume fraction, K-46 Microballoons

Figure 5.35 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 40% volume fraction, K-46 Microballoons
In the case of K-46 microballoons at 40% volume fraction the cracks are more pronounced in the tensile region and are only visible in the high magnification micrograph (Figure 5.35). There are also some microballoons crushed in the compressive region the tensile region (Figure 5.35). This is due to the microballoons directly in the path of the propagating crack.

Figure 5.36 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 50% volume fraction, S-22 Microballoons

Figure 5.37 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 50% volume fraction, S-22 Microballoons
At 50% volume fraction of microballoons there is a transition in the fracture behavior. There are very little micro cracks as can be seen in the Figures 5.36 and 5.37 above. The high magnification micrograph also shows very few micro cracks (Figure 5.37). There is little debonding which is starting to take effect in the fracture process. In the earlier cases of 30% and 40% volume fractions the fracture mechanism was primarily through the propagation of micro cracks which reduced at 50% volume fraction. There are also some voids beginning to take effect in the fracture process.

![Figure 5.38 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 50% volume fraction, K-46 Microballoons](image)

As can be seen form Figure 5.38 there are a few microballoons which have fractured and the fracture is mostly at the interface between the matrix material and the microballoons. The higher magnification micrograph shows that there is a peel off of the layer of matrix material from the surface of the microballoons which suggest that the failure is at the interface (Figure 5.39 B). This could also be some micro cracks starting to develop on the surface of the microballoons This feature is becoming dominant as the
volume fraction of the microballoons increases to above 50%. This feature is observed in both the compressive and tensile regions (Figure 5.39 A & B).

Figure 5.39 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 50% volume fraction, K-46 Microballoons

Figure 5.40 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 60% volume fraction, S-22 Microballoons
Figure 5.41 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 60% volume fraction, S-22 Microballoons

Figure 5.42 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 60% volume fraction, K-46 Microballoons
At volume fraction of 60%, voids started to increase. These voids are trapped air bubbles during fabrication and are shown with arrows in Figures 5.40 and 5.42. During fabrication as the quantity of microballoons increase it becomes difficult to achieve uniform wetting of all the microballoons. There are some air bubbles trapped during mixing of the raw materials and these air bubbles are seen as voids in the micrographs 5.40 and 5.42. These voids start to play a role in the fracture process at high volume fractions of microballoons. Debonding is becoming increasingly evident and there are no micro cracks visible even in the high magnification micrographs (Figures 5.41 and 5.43). The crack encounters microballoons before it can propagate and travels through the boundaries as the interface is the weakest region. When the final fracture occurs the thin layer of matrix material gets peeled off from the surface of the microballoons or the there are some cracks which developed on the surface of the
microballoons (Figure 5.43). Therefore, debonding and peel off are the primary failure mechanisms at higher volume fractions. This is observed in both the compressive and tensile fracture zones.

Figure 5.44 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 65% volume fraction, S-22 Microballoons

Figure 5.45 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 65% volume fraction, S-22 Microballoons
Figure 5.46 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 65% volume fraction, K-46 Microballoons

Figure 5.47 SEM Micrographs of (A) Compressive zone and (B) Tensile zone at 65% volume fraction, K-46 Microballoons
At maximum microballoon volume fraction of 65% the volume fraction of the voids is increasing and therefore there is a reduction in strength as shown in the fracture toughness curves (Figure 5.25). Failure is primarily due to debonding as can be seen in Figures 5.45 and 5.47 above. Figure 5.47 shows that there is debonding around all microballoons and this reason can be attributed to the reduction in fracture toughness with increase in volume fraction of microballoons. In both the tensile and the compressive fracture regions debonding occurred and the specimen fractured. Some of the microballoons which are directly in the crack propagation path have fractured but most of the microballoons were intact (Figure 5.47 A). The same phenomenon was observed for both densities of microballoons, S-22 and K-46.

5.5 Proposed Mechanism

The three main features of interest in the present study glass microballoon filled epoxies are:

1. Inter-particle separation
2. Interface between the microballoon and the epoxy
3. Voids

Inter-particle separation increases with decrease in volume fraction of microballoons from 30% to 65%, with lower volume fraction having more epoxy as compared to higher volume fraction between the micro balloons. At the same time voids are increasing with increase in volume fraction of the microballoons, especially in the case of higher volume fractions, e.g. 60% and 65%. SEM fractographs shown in the previous section suggest that these constituents play a major role in fracture mechanics during 3-point bending tests. It was observed that the number of micro cracks decreased with increasing
microballoon volume fraction. This is evident from Figures 5.48(A)-(E). For example 
micrographs with 30% and 40% volume fractions, Figures 5.48(A) and (B), respectively 
exhibit more number of micro cracks between inter-particle region when compared to 
60% and 65% volume fractions, Figures 5.48(D) and (E), respectively. It was also 
interesting to note that syntactic foams consisting of higher volume fraction showed 
debonding between the epoxy and microballoons. This suggests that different fracture 
mechanisms may be occurring during failure of syntactic foams in 3-point bending tests 
at lower and higher volume fractions.

Present 3-point bending tests show that the fracture toughness decreases with the 
increase in volume fraction of the microballoons. In contrast to the present study, Lee 
and Yee in 2000 showed that the fracture toughness increases with increase in volume 
fraction of the glass beads. The study (Lee & Yee, 2000) was conducted with solid glass 
beads in the volume fraction range of 0% to 30%. They have attributed this to relatively 
fast propagation of the crack through the epoxy matrix at lower volume fractions. 
Whereas at higher volume (30%) fractions, crack propagation was impeded by the 
formation of secondary cracks, which was evident from creation of relatively higher steps 
per unit area in epoxy matrix. These steps look similar to the micro cracks seen in the 
present study. Furthermore, this emphasizes the importance of inter-particle separation in 
the failure mechanism of syntactic foams. In a recent study (Wouterson et al., 2004) with 
hollow microballoons similar observations to the study conducted with solid glass beads 
(Lee & Yee, 2000). It is interesting to note that Wouterson et al., also studied syntactic 
foams with volume fractions ranging from 0 to 20%. No study is available in the 
literature that shows fracture behavior of syntactic foams with volume fraction greater
than 30% using either solid glass beads or hollow glass microballoons. However, it was proposed (Lee & Yee, 2000) that syntactic foam with volume fraction 30% or higher may show a reduction in fracture toughness due to decrease in inter-particle separation.

Figure 5.48 High magnification micrographs showing the change of fracture mechanism from micro cracks to debonding; (A) 30%, (B) 40%, (C) 50%, (D) 60% & (E) 65% volume fractions
Above discussed studies suggest that optimum “inter-particle separation” between epoxy and microballoon is required to have optimum fracture toughness. In view of the present results, the following mechanism for fracture behavior of syntactic foams in 3-point bending tests is proposed:

At 30% and 40% volume fraction of microballoons the fracture mechanism is by the propagation of micro cracks. This is due to the higher inter-particle separation. As the volume fraction of the microballoons increases to 60% and 65%, the inter particle distance reduces and the failure mechanism is primarily debonding. As the number of microballoons in the syntactic foam increase the interfacial area between the matrix and the microballoons increases. This increase in interfacial area results in more microballoons being debonded from the matrix. At 65% volume fraction of microballoons the interfacial area is maximum and is the reason for the lowest fracture toughness at this volume fraction.

In terms of energy (Hull, 1999) the condition for a crack to grow preferentially on a surface, or close to, an interface is that the energy required for a crack propagating at the interface is less than that for a crack propagating through the bulk material away from the interface. This is comprised of two main factors: the first being the surface energy which is determined by the energy and density of atomic bonds that bridge the plane of the crack. Secondly the ease of local plastic and visco-elastic deformation around the crack tip that gives a measure of plastic work in fracture. Thus reduction is surface energy reduces the stress to propagate a crack. Therefore at higher volume fractions due to debonding the energy required for the crack propagation through the interface is lower than the energy required for the crack to propagate through the bulk
matrix and that is the reason for lower fracture toughness at higher volume fractions of microballoons.

The increase in fracture toughness with an increase in density of the microballoons can be attributed to the filler strengthening effect. As the wall thickness of the microballoon increases there are fewer microballoons which are crushed and there is an increase in the strength.

5.6 Fracture Toughness of Syntactic Foams with Rubber Reinforcements

Syntactic foams with rubber reinforcements have been tested using the 3-point bend test and the same procedure was adopted to calculate the fracture toughness as in the case of pure syntactic foams described in section 4.11. Two types of rubber particles have been used and for each type four different densities of microballoons have been used for fabrication. The load deflection curves (Figures 5.49 to 5.52) show that there exists a plastic region due to the presence of rubber particles just before fracture.

Figure 5.49 Load Deflection curve of rubber (45 microns) reinforced syntactic foam with microballoon density 0.22gm/cc
Figure 5.50 Load Deflection curve of rubber (45 microns) reinforced syntactic foam with microballoon density 0.46gm/cc

Figure 5.51 Load Deflection curve of rubber (75 microns) reinforced syntactic foam with microballoon density 0.22gm/cc
Figure 5.52 Load Deflection curve of rubber (75 microns) reinforced syntactic foam with microballoon density 0.46gm/cc

Figure 5.53 Variation of fracture toughness with microballoon density for both types of rubber particles
The fracture toughness is higher for syntactic foams with larger rubber particles. This is evident from the above Figure (Figure 5.53). At microballoon density of 0.22 g/cc the curves intersect each other. This is due to the presence of higher volume fraction of voids present in the syntactic foam specimen. Considering more number of data points might resolve the ambiguity observed. At high volume fractions of 63% and inclusion of 2% rubber particles controlling void fraction is a challenging task. The overall trend is evident and shows that the fracture toughness reduces with increasing volume fraction of the filler material (microballoons and rubber particles). In the first section of this chapter (Section 5.1) it was observed that the density of these rubber reinforced syntactic foam slabs is much higher than those of pure syntactic foam slabs (Figure 5.3). Now it would be interesting to compare the fracture toughness characteristics between the two. The fracture toughness of syntactic foams with rubber reinforcements is compared to pure syntactic foams without rubber reinforcements in the following Figure (Figure 5.54).

![Figure 5.54 Comparison of fracture toughness with and without rubber reinforcements with variation in microballoon density](image-url)
From the Figure 5.54 it can be seen that syntactic foams with rubber reinforcements have much higher fracture toughness than those without rubber reinforcements. The foam with the 45 micron rubber particles converges with the pure syntactic foam curve. This is due to the higher volume fraction of voids present in that particular syntactic foam slab. As seen in the first section, Section 5.1 of this chapter the addition of rubber particles increases the density by 14% but increases the fracture toughness by 35%. The reason for rapid increase of fracture toughness when the microballoon density increases from 0.32 g/cc to 0.38 g/cc can be understood by considering more data points in-between. The micrographic analysis of the rubber reinforced syntactic foams is discussed below.

5.7 Micrographic Analysis

SEM analysis was performed on the sections of the fracture surface after coating them with a layer of gold sputter. S-22 and K-46 density fracture specimens were analyzed for their fracture features. It was found throughout the fracture surface that there are numerous number of voids and the cracks passed through the voids (Figure 5.55B).

Figure 5.55 SEM micrograph of syntactic foam fabricated with S-22 microballoons and 45 micron rubber particles (A) Compressive, (B) Tensile region
Figure 5.56 SEM micrograph showing rough fracture surface due to inclusion of rubber particles (rubber particles 45 microns, S-22 microballoons)

Figure 5.57 SEM micrograph showing ductile fracture features due to the presence of rubber particles (rubber particles 45 microns, S-22 microballoons)
The Figure above (Figure 5.55) shows extensive debonding and some voids present in the material. The fracture features in these micrographs (Figures 5.55 to 5.57) are similar to features observed in the case of pure syntactic foams. The only difference is the presence of rubber particles inducing plastic deformation before the sample fractured (Figures 5.48 to 5.52). The presence of rough fracture surface in Figure 5.57 indicates that the failure is at the rubber matrix interface.

5.8 Proposed Mechanism

Rubber particles are added to composite materials to improve their crack propagation properties. Debonding is the significant phenomenon here but these materials having rubber particles have higher fracture toughness values than pure syntactic foams. This is because the rubber particles come in the way of the crack and for the crack to propagate the rubber particles need to fracture. It can be observed form the Load Displacement curves of these specimens (Figures 5.48 to 5.51) shows that just before fracture there is a little elastic region where yielding takes place. This is because of the rubber particles coming in the way of propagating crack resulting in elastic deformation. The SEM micrographs (Figures 5.55 to 5.57) also show a fracture surface which is very rough and indicative of a ductile fracture surface. This increase in the fracture toughness values of rubber reinforced foams can be attributed to the rubber particles coming in the way of propagating crack. Figures 5.56 and 5.57 show the fracture surface and the rough region marked is indicative of a ductile fracture. The failure of the foam is due to debonding like in the case of pure syntactic foams. In all the micrographs shown above (Figures 5.55 -57) debonding can be seen as the reason for failure.
CHAPTER 6

CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions Generated from the Study of Syntactic Foams with Microballoons

Syntactic foam samples have been fabricated by varying both the volume fraction of the microballoons and also their density. Four densities of microballoons have been used with their volume fractions ranging from 30% to 65%. The conclusions drawn from the 3-point bending tests are summarized as follows:

1. Increasing the volume fraction of the microballoons resulted in a decrease in the values of fracture toughness. The decrease was uniform for all the four densities of microballoons tested in this thesis work.

2. Increase of density of microballoons at each volume fraction increased the fracture toughness uniformly.

3. SEM analysis on the fracture surfaces showed that at low volume fractions there is formation of micro cracks. These secondary micro cracks when they meet result in a toughening mechanism by hindering the propagation of the primary crack. At higher volume fractions due to reduced inter-particle distance debonding occurs and the samples fail at lower peak loads.

4. It was found that at high microballoon volume fraction of 65% voids start playing a significant role in the fracture process. This is the maximum packing fraction for the microballoons and above this value it would be difficult to achieve complete wetting of the microballoons.
6.2 Conclusions Generated from the Study of Syntactic Foams with Rubber Reinforcements

Syntactic foams have been fabricated with rubber reinforcements (2% rubber and 63% microballoons) to study their effect on the fracture behavior. The 3-point bend tests have been conducted and the following conclusions have been drawn:

1. Syntactic foams fabricated with bigger rubber particles showed more density and fracture toughness.
2. Syntactic foams with rubber reinforcements had higher density and fracture toughness than syntactic foams without the inclusion of rubber reinforcements.
3. The load displacement curves showed plastic deformation just before the specimen fractured.
4. SEM studies showed that in both sizes of rubber particles, the rubber particles and the microballoons were not uniformly mixed within the resin matrix. Some micrographs showed ductile fracture features.

6.3 Recommendations of Future Work

Incorporation of rubber particles tends to improve the crack propagation and damping properties of syntactic foams. Therefore, syntactic foams with higher volume fraction of rubber particles need to be fabricated and tested to find the optimum volume fraction of microballoons. When manufacturing syntactic foams with rubber particles it was found that significant volume fractions of voids are present in the syntactic foam structure. This resulted in the large sized rubber particles (75 microns) having lower densities when compared to slabs fabricated with smaller rubber particles (45 microns). Therefore, experiments need to be done with more data points. Syntactic Foam slabs need to be fabricated with volume fractions ranging from 0% to
65%. This should be done for more number of microballoon densities to find a trend in the fracture behavior. Finite element models need to be developed to verify the experimental results. As syntactic foams are potential candidates in aerospace applications, experiments need to be conducted to determine the fire performance properties.
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VITA

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