Toughening of low-weight foam-based composites

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Toughening of Low-weight Foam-based Composites

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ABSTRACT

Various industries, incl. defense, aerospace and automotive, are spending large budgets on the development of lightweight materials. Especially, sandwich composites gain increasing attention due to their high strength-to-weight which allows for a structural weight reduction compared to conventional metallic structures. Sandwich composites comprise of fibrous outer layers and a core material. Syntactic foam, comprising of a binder and hollow microspheres, would be an attractive material to be used as the core material since it is a lightweight material with tremendous compressive strength, low moisture absorption, and low radar detectability. However, the major disadvantage of syntactic foam is its brittle behavior under mechanical loading. Due to its brittleness, it has a low resistance to the formation and propagation of cracks, limiting the number of advanced applications of syntactic foam.

To resolve this problem, three different toughening approaches have been studied. The first approach involved a study on the effect of porosity on various specific properties of syntactic foam, including specific fracture toughness. Results showed that a maximum specific fracture toughness was obtained around 30 vol% of microspheres content. The maximum was independent of the type of microspheres used and was attributed to a change in the dominating toughening mechanism from step structures towards debonding of microspheres.

The second approach involved the inclusion of short carbon fibers. Results show that inclusion of 3wt% of carbon fibers in a syntactic foam containing 30 vol% of hollow phenolic microspheres increases the tensile strength, Young's modulus, plane strain fracture toughness, and critical energy release rate by 40, 115 and 95, and 90% respectively. Such property improvements are considered impressive in polymer composites. Fractured and debonded fibers, leading to increased matrix plasticity, step structures and microsphere debonding are believed to be responsible for the increase in tensile and fracture properties.

The third approach encompassed the inclusion of nanoclay layers. Despite a 13% reduction in the tensile strength, results showed an increase in the Young's modulus of 19.5% for 3 wt% of nanoclay content. For the fracture behavior, a synergistic behavior between the nanoclay and microspheres was observed for specimens containing 1 wt% nanoclay. Both the microspheres and (agglomerates) of nanoclay caused the presence of toughening mechanisms like i.e. crack pinning, matrix deformation, and debonded microspheres.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

A	Cross-sectional area	[mm ²]
a	Crack length	[mm]
d	Fiber diameter	[μm]
E	Modulus	[N/mm ²]
F	Force	[N]
G	Shear Modulus	[N/mm ²]
K _{Ic}	Critical Stress Intensity Factor	[MPa.√m]
L	Fiber length	[mm]
m	Initial slope of load vs. displacement curve	[-]
N	Number of fibers	[-]
P	Load	[N]
R	Strain rate	[min ⁻¹]
ρ	Density	[g/cm ³]
R	Toughness	[J/m ²]
s	Fiber aspect ratio	[-]
S	Support span	[mm]
σ	Stress	[N/mm ²]
t	Sample thickness	[mm]
T _g	Glass transition temperature	[°C]
τ	Shear Strength	[N/mm ²]
v	Velocity	[m/s]
Y	Shape factor	[-]
y	Time	[s]
W	Sample width	[mm]
χ	Volume fraction	[-]
z	Cross-head speed	[mm/min]

Subscript

b	Bending
c	Compression
crit	Critical
d	Interfacial debonding
f	Flexure
fib	Fiber
fr	Friction
m	Matrix
po	Pull-out
r	Redistribution of strain energy
s	New surfaces
t	Tensile
v	Void
y	Yield

Abbreviations

3PB	Three Point Bending
ASTM	American Society for Testing and Materials
DMA	Dynamic Mechanical Analysis
FLD	Fiber Length Distribution
FOD	Fiber Orientation Distribution
LEFM	Linear Elastic Fracture Mechanics
MS	Micro-shear
MSE	School of Materials Science and Engineering
NCRSF	Nanoclay-Reinforced Syntactic Foam
NTU	Nanyang Technological University
OM	Optical Microscopy
PFPC	Particulate-Filled Polymer Composite
ROM	Rule of Mixtures
SCF	Short Carbon Fibers
SEM	Scanning Electron Microscopy

SENB	Single Edge Notched Bend
SFRE	Short-Fiber-Reinforced Epoxy
SFRP	Short-Fiber-Reinforced Polymer
SFRSF	Short-Fiber-Reinforced Syntactic Foam
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOM	Transmission Optical Microscopy
vol%	Volume Percentage
wt%	Weight Percentage

CHAPTER 1

INTRODUCTION

1.1 Background

In many industries, there is an ongoing search for lighter structures. In particular the transportation industries, i.e. automotive, marine and aerospace, spend huge budgets on their R&D activities to reduce the weight of cars, boats and aircraft, respectively. One of the major driving factors for this development is the ever increasing oil price. Reducing the weight of transportation vehicles would mean an increase in the fuel efficiency. Besides a better efficiency, the lower weight also contributes to a 'greener' environment as it will reduce the exhaust emissions.

Figure 1 shows that there are a huge number of materials available for structural applications. Each type of material exhibits a certain range of strength-density relationships. As the density changes for each type of material, a fair comparison among the various materials is not allowed. The performance of these materials can only be compared if their so-called specific properties are being considered.

Improving specific properties is the key in reducing the weight of structural applications. Improving the specific properties can either be improved through an increase in the material property or through a reduction in the density. The former is often

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Figure 1: Strength-density envelopes of various materials

Table 1.1: Specific properties of various materials

Material	σ/p ($10^3 \cdot \text{m}^2/\text{s}^2$)	E/p ($10^6 \cdot \text{m}^2/\text{s}^2$)
Steel 0.2 carbon	99	27
Aluminum 2024-T3	98	25
Ivory	114	9.2
Birch wood	211	25
HM-Carbon (M40)	749	107
HM-Aramid	1210	39
E-glass	669	14

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achieved through materials science and engineering applied onto the structural material while the latter is achieved by replacing the material with a more advanced material having similar or even better properties at a lower density. As most metallics have been around for decades, it is not expected that research on these materials will lead to major improvements in the reduction of the strength-to-weight ratio. Major improvements are, however, expected from the introduction of new advanced materials. Some specific properties of various materials, taken from [1], are given in Table 1.1. It is clear from Table 1.1 that composite materials comprising of synthetic fibers in a polymer matrix are highly suitable to replace the conventional metallic structures. Introduction of composite materials in primary structures, the weight of the structure will be reduced while maintaining or improving existing strength levels.

Figure 2: Materials used in the future Boeing 787 Dreamliner

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For this reason, aerospace manufacturers are increasingly using composite materials. For example, 50% of the structure of the new Boeing 787 'Dreamliner' will comprise of composites, see Figure 2 [2], compared to only 10% for the Boeing 777. The high usage of composite materials is expected to reduce the weight by 10,000 lbs compared to a structure with conventional materials. Besides the reduction in weight, the use of composite materials will have additional advantages over conventional metallic structures, including lower exhaust emission, integration of various functions into one structure and reduced maintenance costs due to composite materials being less prone to fatigue.

A sandwich composite is an attractive composite structure to be used for structural applications in the marine and aerospace industries. Sandwich composites are made up of fibrous skin layers and a core material. The core material can be made of various materials, including balsa wood, foam and honeycomb. Recently, it has been proven that a special type of foam, namely syntactic foam, is a promising material to be used as the core material in sandwich composite due to creation of a damage-tolerant structure. Additional advantages of the use of syntactic foam as the core material are its cellular structure leading to a lightweight material with tremendous compressive strength, low moisture absorption, and low radar detectability.

Syntactic foam is a ternary material comprising of hollow spheres and a binder. Incorporation of a thermosetting matrix, i.e. epoxy resin, in syntactic foams results in many useful properties for structural engineering applications, such as a high modulus

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and failure strength, low creep, and good performance at elevated temperatures. However, the structure of such thermosetting polymers also leads to one highly undesirable property in that thermoset materials are relatively brittle materials, with a poor resistance to crack initiation and growth. The low resistance to crack initiation and growth limits the number of applications of these materials in areas prone to high stresses and shock loading.

1.2 Problem Statement

In order to increase the number of advanced applications of syntactic foam-based composites, it is essential to increase the toughness of these types of foams. The objective of this thesis is to improve the toughness of foam-based composites. Besides the improvement in the fracture properties, the increase in toughness should not be accompanied by detrimental mechanical and thermal properties. The results of various reinforcements of syntactic foam and their effect on the mechanical, fracture and thermal properties will be discussed in light of the microstructure and fracture mechanics.

1.3 Outline of the Study

In order to achieve the objective, as set in the previous paragraph, the work undertaken is outlined in Figure 3.

Introduction

Figure 3: Project Outline

Each of the studies presented in Figure 3 will be discussed in more detail below:

- A) Development of a repeatable processing technique to produce high quality syntactic foam, regardless of the type and amount of microspheres used. The development required a thorough understanding of the characteristics and handling of the various components of syntactic foam and the available processing techniques for composite materials.
- B) The effect of the microstructure on the mechanical, fracture and thermal properties was studied. The microstructure was varied by changing the type and amount of microspheres in the syntactic foam. Various properties including tensile strength, Young's modulus, compression yield strength, compression

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modulus, flexure strength, flexure modulus, critical stress intensity factor, critical energy release rate, thermal stability and the glass transition temperature were characterized, and the significance of the results was discussed.

C1) A method to process short carbon fiber-reinforced syntactic foam was developed.

The effect of the fiber content as well as the fiber length on the mechanical, fracture and thermal properties was investigated. Microscopy was employed to characterize the toughening mechanism present.

C2) A method to process nanoclay-reinforced syntactic foam was developed. The

effect of the nanoclay content on the mechanical, fracture and thermal properties was investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 Foams

Foam is a material which is formed by entrapping a large amount of air bubbles in a liquid or solid. The physical and mechanical properties of the foam can be tailored by changing the amount of gas in the material. Foams can have excellent heat- and sound-insulation properties due to their high resistance against mass transport. Other foams have the ability to absorb a lot of energy, which makes them very useful in cushioning and packaging applications [3].

Foam materials are widely used nowadays. Some examples of foam materials are seat cushions, foam tape, Styrofoam tea cups, packaging materials, insulation foam, liners of helmets, etc. Foams can be made of various materials, incl. metals, elastomers, plastics, ceramics and other materials with various porosities. In general, foam materials can be divided into three different categories, namely open cellular, closed cellular, and syntactic. Each category of foam will be discussed in the following subparagraphs.

2.1.1 Open-cell Foams

Open cellular foams have interconnected pores or cells; see Figure 4 [3]. Typically, open cellular foams exhibit a porosity of about 80-90 vol%. The high porosity which leads to a dramatic reduction in weight compared to the un-foamed material makes open-cell foams a suitable material for ultra-lightweight applications. Besides their low weight, open cell foams also feature high gas and vapor permeability. Depending on the material that is being foamed, the final product will be flexible or rigid. The flexible foams are able to bend easily without cracking. This makes flexible foams ideal for shock absorbing applications. On the other hand, rigid foams feature a matrix with limited flexibility.

Figure 4: Open-cell foam

2.1.2 Closed-cell Foams

Closed cellular foams, see Figure 5, do not have interconnected pores or cells. The cell wall acts as a barrier to gases and fluids, although gases may pass through the cell wall by the slow process of diffusion. The barrier capabilities of closed foam make it an excellent insulation material. Besides insulation, closed cell foam also features excellent floating capabilities. Due to the entrapment of gases, the density of the foam is often below the density of water. Combined with the barrier properties of closed cell foams, it is thus able to float on water which makes closed cell foams a suitable material for marine applications.

Compared to open cell foams closed cell foams often show a higher density. The higher density is caused by the higher number of cell walls, requiring more material, and therefore, more expensive. The advantages of the closed-cell foam compared to open-cell foam include its strength, greater resistance to the leakage of air or water vapor, and a higher R-value. R value insulation ratings are used to measure insulations ability to resist heat flow. The higher the R value, the more effective it is.

A special category of closed cell foams are the so-called syntactic foams. Syntactic foams feature a closed cell structure but differ from the conventional closed cell foams in the sense that the porosity is created through the dispersion of hollow spheres into the matrix. As the filler material is often different from the matrix material, syntactic foams are classified as ternary systems whereas conventional closed foams are classified

Figure 5: Closed-cell foam

[Courtesy Shinko Wire Company]

as binary systems. Syntactic foams will be discussed in more detail in the following paragraph.

2.2 Syntactic Foam

2.2.1 Introduction to Syntactic Foam

Syntactic foam was developed in the early 60's [15-25]. Syntactic foams are a special kind of particulate composite materials made by a matrix ('binder') and a gas-filled aggregate ('filler') consisting of hollow spherical microspheres, see Figure 6. These

Figure 6: Concept of syntactic foam

composite materials are classified as foams since they possess a structure formally similar to that of a cellular, gas-expanded, solidified liquid. The term syntactic, which originates from the Greek word 'syntaktikos', (= orderly disposed system) indicates a constructed foam, in the sense that the material is manufactured by a specific mixing procedure of fillers and binders with appropriate volume fractions. The filler is randomly dispersed in the matrix, creating a homogeneous exhibiting isotropic macroscopic behavior. Since the spheres have continuous shells, the final material can be considered as a closed-cell foam. An SEM image of syntactic foam is shown in Figure 7.

The advantages of syntactic foam over the conventional foams are its mechanical properties of syntactic foam which are several orders of magnitude higher than the properties of the lighter (traditional) foams. The foamed materials can serve as the core material in sandwiched composite structures with fiber-reinforced polymeric facings, see Figure 8. Unlike most other foams, no chemicals are required to create the porosity. In addition, syntactic foam is a material whose density before curing is the same as that after

Figure 7: SEM image of syntactic foam

Figure 8: Sandwich composite with syntactic foam core

curing. Such predictability and attribute are advantageous in the manufacturing process in high performance structures used in the aerospace, automotive and marine industries.

2.2.2 Materials

Syntactic foams are classified as being ternary systems as the matrix and gas-filled aggregate are usually made of different materials. This paragraph discusses the different materials that can be used for the filler and binder of syntactic foams.

a) Filler

The filler used in syntactic foam are hollow spheres. Figure 9 shows an example of hollow microspheres. Hollow spheres are available in various diameters ranging from millimeters [4] to nanometers [5]. The choice of the sphere size depends on the proposed application. As hollow nanospheres have only been developed recently, most of the literature report on syntactic foams containing microspheres or macrospheres.

Depending on the type of microsphere, hollow microspheres have a diameter ranging between 5-250 μm and a wall thickness in the order of 1-5 μm . The advantage of using hollow microspheres is the reduction of the weight of the composite with increasing hollow microspheres content. It should be noted that the reduction in weight is only obtained if the density of the microsphere is lower compared to the density of the binder.

Figure 9: SEM image of hollow microspheres

The wall material of the hollow sphere can be made of ceramic [6,7,8], carbon [9,10,11], glass [12], polymer[13,14], or metal [15]. According to Shutov [16], it is important that the microspheres are spherical, non-cohesive, strong, intact, resistant to moisture and chemicals, and hydrolytically stable. Spherical fillers are preferred as they tend to roll easily over one another. The rolling of the microspheres improves the flow of many materials to which microspheres are being added. In addition, a spherical geometry is preferred as it allows the best packing factor and hydrostatic compression strength.

Glass microspheres are most frequent used due to their mechanical strength, smoothness, regularity of the surface, good wetting characteristics and low viscosity of the resulting foam, all this combined with well-established production procedures and

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low cost. However, [16] report that recently it has been shown the use of carbon microspheres could lead to even better properties compared to syntactic foams containing hollow glass microspheres. The syntactic foams can be used at higher operation temperatures, and are more capable of withstanding hydrostatic pressure, for the same concentration of filler. Furthermore, [16] reports that the smaller the carbon microspheres, the stronger are the resulting foams. A similar conclusion was drawn by d'Almeida [17]. D'Almeida studied the effect of the diameters of glass microspheres on the mechanical behavior of syntactic foam. From the study, the conclusion was drawn that microspheres with smaller diameters resulted in a higher specific stress and a higher specific modulus.

b) Binder

According to [16], the ideal binder used in syntactic foam should comply with the following requirements:

- a) Low viscosity to facilitate rapid filling of the mold,
- b) Easily controlled gelation time to prevent lamination of the composite,
- c) Small exothermal effect during curing,
- d) Low curing shrinkage
- e) Good adhesion and wettability to the filler
- f) Compatibility with modifiers and fillers, including diluents, plasticizers, dyes, and flame retardants

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Most of the reports found in the literature report about epoxy-based syntactic foam [25-27]. The term 'epoxy' refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms, see Figure 10. The simplest epoxy is a three-member ring structure known by the term 'alpha-epoxy' or '1,2-epoxy'.

Epoxy resins are formed from a long chain molecular structure similar to vinyl ester with reactive sites at either end. In the epoxy resin, however, these reactive sites are formed by epoxy groups instead of ester groups. The absence of ester groups means that the epoxy resin has particularly good water resistance. The epoxy molecule also contains two ring groups at its centre which are able to absorb both mechanical and thermal stresses better than linear groups and therefore give the epoxy resin very good stiffness, toughness and heat resistant properties. Figure 10 and Figure 11 below show the idealized chemical structure of a typical epoxy.

Figure 10: Idealized Chemical Structure of a simple epoxy

Figure 11: Idealized chemical structure of a typical epoxy (Bisphenol-A)

According to [26], the advantages of epoxies as the binder in syntactic foam, are its high strength and modulus, low levels of volatiles, excellent adhesion, low shrinkage, and good chemical resistance, and ease of processing. Their major disadvantages are brittleness and the reduction of properties in the presence of moisture. The processing or curing of epoxies is slower than polyester resins. The cost of the resin is also higher than the polyesters. Depending on the type of epoxy resin, processing techniques include autoclave molding, filament winding, press molding, vacuum bag molding, resin transfer molding, and pultrusion. Curing temperatures vary from room temperature to approximately 180 °C. The use temperatures of the cured structure will also vary with the cure temperature. Higher temperature cures generally yield greater temperature resistance. Cure pressures are generally considered as low pressure molding from vacuum to approximately 700 kPa.

Relatively little has been reported about other types of resin-based syntactic foams. Fine et al. [18] report about a syntactic foam incorporating polyphenylene ether (PPE), a thermoplastic resin as the matrix. PPE is used in order to create a syntactic foam which can be operated at high temperature applications. Gladysz et al. [19] incorporated a bismaleimide to create a syntactic foam for high temperature applications. Huang et al.

Figure 11: Idealized chemical structure of a typical epoxy (Bisphenol-A)

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have reported some work on phenolic-based syntactic foam [20] whereas Bruneton et al. [21] report the mechanical behavior of a carbon/carbon syntactic foam. However, the majority of the research on syntactic foam involves the use of epoxy resin.

2.2.3 Mechanical Behavior of Syntactic Foam

Since its introduction in the 1960's many mechanical aspects of syntactic foam have been studied extensively. This subparagraph highlights the mechanical behavior and some important properties of syntactic foam.

a) Compression properties

As outlined in the introduction, syntactic foam was initially used for its impressive compression properties. The compression properties have been reported extensively by various researchers [22 - 37]. A comprehensive explanation of the compression behavior of syntactic foam was given by Bunn and Mottram [32]. Bunn and Mottram identified three different regions which are shown in a typical compression stress-strain curve of syntactic foam, see Figure 12. In region one, a linear curve in the stress-strain curve is observed. In region one, the syntactic foam behaves like an elastic material. Removal of the compressive load makes the material return to its original dimensions. Region two starts from the point where the compressive stress reaches its

Figure 12: Compressive stress against engineering strain for syntactic foam

maximum and stretches over a region where the compressive stress of syntactic foam is fairly constant at about 95% of maximum of compressive stress. The horizontal region is characterized as the collapse region where more and more microspheres collapse under the compressive load.

The engineering strain at the end of the plateau can be quite large, around 25%. Due to the collapsing of the microspheres, the material gets denser. As the material gets denser, it can resist higher compressive loads and that explains why the curve rises in region three.

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Besides the general behavior under compression, [32] reports on the uniaxial compression properties of a syntactic foam system with varying volume fractions of phenolic microballoons. Short-term compression tests showed that the compression yield strength and initial tangent modulus of elasticity were linearly dependent on the volume fraction of microballoons. Both the compression yield strength and initial tangent modulus decreased with increasing filler content. A similar decreasing trend in the compressive yield strength with increasing filler content as reported by [32] was observed by Palumbo et al. [25], Almeida [17] as well as Lin and Jen [26]. Palumbo et al. studied the mechanical properties of a hollow glass microsphere-filled epoxy resin composite system as a function of the weight content of hollow microspheres ranging from 0 to 15.38 wt%. The failure of the syntactic foam was attributed to extensive debonding between the epoxy matrix and the hollow glass microspheres. [25] concluded that the extent of exposure of fractured microspheres on the fracture surface suggested that by acting as regions of local weakness and stress concentrations their function is more important than simply that of reducing the proportion of resin in the composite. Further it is shown that the experimental results do not coalesce with existing theoretical models. Possible explanations for the mismatch between the theoretical and experimental are the possible mechanical destruction of hollow microspheres in the course of the composite preparation or possible residual thermal stresses around the glass microspheres as a consequence of the inevitable mismatch between coefficients of thermal expansion.

Studies performed by Gupta et al. [23,24] showed the effect of the specimen size on the compressive properties of syntactic foam. The specimen's behavior during

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compression showed remarkable difference with respect to the aspect ratio. In specimens having high aspect ratio, possessing sufficient thickness, cracks were found to propagate through the specimen center to the opposite face, giving rise to shear type of failure, see Figure 13a. However, a similar crack propagation event yielded wedge-shaped fragments from sidewalls in the low aspect ratio specimens. Besides the difference in fracture behavior, [23,24] reported that for an aspect ratio of 0.6, the decrease in compressive stress was absent. The compressive stress remained constant until densification occurred. For specimens with an aspect ratio of 0.4, a continuous increase in the stress for all regions was observed.

Figure 13: Schematic representation crack origination and propagation for specimens with (a) high aspect ratio; (b) low aspect ratio.

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[27] reports that in case of higher aspect ratios, the effect of the shear component of the applied compressive stress is prominent, whereas in lower aspect ratio specimens true compression prevails. This explains why ASTM standard D695-96 [38] recommends specimens with an aspect ratio of 0.5.

b) Tensile Properties

Compared to the compressive properties, less data has been published on the tensile properties of syntactic foam [33,34,39-42]. [33,34] report on the tensile properties of Tencara 2000™, a commercial available syntactic foam. The response of the syntactic foam under tension was perfectly brittle as the tensile samples ruptured on a section perpendicular to the loading axis. The brittleness was caused by the addition of stiff microspheres which reduced the ductility of the overall system.

[42] reports about the effect of the amount of microspheres on the tensile properties of syntactic foam. The effect of the microspheres content on the stress-strain curve, as reported by [42], is shown in Figure 14a and Figure 14b. It was observed that as the volume fraction of the microballoons in the epoxy matrix increased, the failure stresses and strains decreased, see Figure 14a. In addition, the increase in microspheres content lead to a reduction of the Young's modulus and an increase of the elastic strain at a given stress, see Figure 14b. The results presented by [42] had been previously explained by Krstic and Erickson [43] who attributed the result to a crack opening displacement caused by the presence of radial and/or annular cracks associated with pores.

(a)

(b)

Figure 14: Tensile properties for syntactic foam with different microballoon content; (a) tensile strength, (b) Young's modulus.

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Bardella and Genna [41] report more extensive results on the effect of the microspheres content on the tensile properties. [41] reports that the trend between the Young's modulus and filler content is depending on the type of microspheres being dispersed in the matrix. Based on the results presented by [41], it can be concluded that the conclusions drawn by [42] are only valid for the specific type of microspheres and matrix used. Consequently, it can be concluded that the theory derived by [43] only applies to microspheres that induce a downward trend in the Young's modulus with increasing filler content.

McBride and Shukla [40] report about the tensile strength of a lightweight concrete using ceramic microspheres as a primary aggregate. It was shown that the tensile strength drops by about 35% when hollow microspheres were added to the mixture. However, the tensile strength seemed to be constant for larger amounts of microspheres. The drop in the tensile strength was attributed to a poor microsphere/binder interface.

c) Flexure properties

Similar to the tensile properties of syntactic foam, reports on the flexural properties of pristine syntactic foam are scarce [44-49]. Depending on the application and configuration of the syntactic foam, various standards test methods can be used to obtain the flexure properties of syntactic foams [50-52].

Figure 15: Load vs. Displacement curve of a syntactic foam under three point bending.

A typical response of a syntactic foam under three point bending is shown in Figure 15, as taken from [19]. The behavior of the syntactic foam, as shown in Figure 15 can be qualified as being brittle. After achieving the maximum flexural load, an almost vertical drop in the load is observed. Others [33] report the existence of a so-called softening tail after the vertical drop in the load. The softening tail indicates the possibility of syntactic foam behaving quasi-brittle. The various response is attributed to the different compositions of the syntactic foam. Typical values for the core shear modulus, G , and core shear strength, τ , are 229 MPa and 13 MPa, respectively. It should be noted that these values are depending on the composition of the syntactic foam.

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Gupta et al. [45] studied the flexural properties of syntactic foam core sandwich composites in relation to the radius ratio of the microspheres. Based on three- and four-point bending tests on syntactic foams with varying radius ratio, they concluded that the failure of syntactic foam core sandwich composites is governed by tensile properties of the foam core and the strength is not affected by the microsphere radius ratio. Shear failure takes place in short beam shear tests, which makes the microsphere radius ratio an important factor in determining the strength of the sandwich composite.

d) Fracture properties

The reported works on the fracture behavior of syntactic foam focus on the impact behavior of syntactic foam [53-55]. Kim and Oh performed impact testing by dropping a dead weight from a certain height onto cylindrical specimens with varying diameter. It was observed that for syntactic foam containing 39 parts by volume of hollow microspheres, the impact stress had reduced compared to plain epoxy resin. Kim and Oh reported an average impact stress between 20-40 MPa. The impact stress was not affected by the different diameters.

Hiel et al. [55] show the excellent damage tolerance capabilities of foam-based sandwich composites with a syntactic foam core. The damage remains localized due to the energy-absorbing capacity of the glass microspheres. The imprint formed at the facing is localized as well and visible to the unaided eye which is ideal for maintaining and securing the safety of the structure. The damage is visible due to local delamination over an area which is slightly elliptical.

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Benderly et al. are one of the few that studied the fracture toughness of syntactic foam [44]. Their research work focused on the fracture toughness of several epoxy based syntactic foams, as affected by foam composition. The parameters of interest were the curing agent type (anhydride and amine) and elastomer type and their quantity. For the anhydride curing agents studied, the addition of elastomer improved the fracture toughness, and no reduction in flexural strength was observed upon elastomer addition. Examination of the fracture surface showed that the failure mechanism varied with foam composition, from crack propagation around the microballoon filler to crack propagation through the filler, possibly explaining the strength results. For a syntactic foam cured with a cyclo-aliphatic amine curing agent, the addition of elastomer did not significantly affect the fracture toughness. Examination of the fracture surface showed that the failure mechanism for the syntactic foam compositions with and without added elastomer was crack propagation through the matrix rather than through the microballoon filler.

2.2.4 Applications of Syntactic Foam

Due to its closed cell structure, syntactic foams absorb only minimal amounts of liquid [29,56]. The minimum liquid absorbance, together with its low density, makes syntactic foam an ideal material to be used in the marine industry. Syntactic foams are used to make floats and buoys. An example is Eccofloat® by Trelleborg Emerson & Cuming, Inc., see Figure 16. As syntactic foams feature impressive compressive properties, syntactic foams have been used extensively for deep sea applications, like i.e. structure of underwater rescue vehicles, structure of submarines, bulkheads, diving suits, insulation of underwater pipe lines, and equipment for raising sunken ships.

Figure 16: Eccofloat [57]

Syntactic foams are not only used for marine and deep sea applications. Syntactic foams are also widely used in civil and industrial engineering. Syntactic foams can be used in cements and large-diameter municipal water installations. Syntactic foams are also a favorite material among pattern makers, since syntactic foams offer the workability of wood without the orthotropy caused by a grain. Syntactic foam is excellent for checking tool paths, building mock-ups, and making molds for high-performance laminated composites.

Syntactic foams are increasingly used in the aerospace industry, see Figure 17c. Especially, due to the increasing fuel prices, there is an increasing demand for

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lightweight materials. Syntactic foam is mostly used as the core material in sandwich composites. Syntactic foams are an excellent replacement of honeycombs, especially in parts of the structure that are highly contoured or involved with communication, navigation, or radar antennas. An additional advantage of using syntactic foam in structures involving navigation is its microwave transparency caused by the air present in the microspheres. Syntactic foam hardly interferes with the microwaves sent/received by the aircraft making it an excellent material to be used in radomes.

Finally, syntactic foams can be found in many sports attributes. Syntactic foams are used for their lightness and mostly excellent compressive properties. For the past few years, Adidas is using syntactic foam in their soccer balls, see Figure 17. For the first introduced during Euro 2000, the Terrestro Silverstream featured an outer layer made from ergonomically crafted syntactic foam panels in polyurethane. Inside the ball's casing was a layer of closely compressed micro balloons filled with gas, which distributed the impact of the strike (from the foot or head) evenly, making it more precise and giving it a calculable, consistent, and faster flight path. Other sports where syntactic foams are used are archery (limb), car racing (panels), sailing.

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Figure 17: Various Applications of Syntactic Foam; (a) Soccer ball, (b) structure of submarines, (c) aircraft radomes, (d) missile heads.

2.3 Toughening of polymers

2.3.1 Introduction to Polymer Toughness

According to [58], fracture can be defined as the creation of new surfaces within a body through the application of external forces. For a fracture to occur, a crack must be created, initiated and propagated. The whole fracture process is complex involving a continuous and evolving sequence of mechanical and thermal interactions in the various zones surrounding the crack tip.

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A fracture can be classified as brittle or ductile depending on the rate of crack propagation and the amount of the resulting deformation. Brittle fracture, see Figure 18, occurs by rapid crack propagation and without appreciable macroscopic deformation. Another feature of brittle cracks is that the cracks run close to perpendicular to the applied stress leaving a relatively flat surface. Perkins [59] explains that in brittle fracture, localized crazes initiate, grow, and break down to give cracks at stresses below those necessary to cause bulk shear yielding. This explains why brittle fracture requires only a relatively low value of fracture energy. On the contrary, in ductile fracture, see Figure 18, extensive plastic deformation takes place before fracture is observed. Brittle as well as ductile behavior is observed in polymers. The occurrence of brittle or ductile behavior depends on the structure of the polymer and its environment of operation.

Figure 19 show that cracks under load can be opened in different ways. In mode I the crack is opened perpendicular to the fracture surfaces. In modes II and III the displacements occur in the plane of the crack. Mode I cracking is most widely used in the linear elastic fracture mechanics (LEFM).

The fracture toughness is one of the most important properties in a structural material. According to [60] fracture toughness can be defined as a quantitative way of expressing a material's resistance to brittle fracture when a crack is present. If a material has a large value of fracture toughness it will probably undergo ductile fracture. Brittle fracture is very characteristic of materials with a low fracture toughness value.

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Figure 18: Brittle and ductile stress-strain curves [61]

Figure 19 Various cracking modes

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It has been shown by various researchers that the fracture toughness of particle-reinforced brittle matrices can be estimated by using LEFM [62,70-73]. A test method for the determination of plain strain fracture toughness is described in the ASTM standard D5045 [63]. A pre-requisite of applying the LEFM onto particulate reinforced composites in order to determine the fracture toughness, is the existence of a plane-strain condition at the crack tip. If the specimen dimensions comply with Equation 2.1 [64], it can be assumed that a plane strain condition at the crack tip exists:

$$t, a, (W - a) \geq 2.5 \frac{K_C^2}{\sigma_y^2} \quad (2.1),$$

where t , is the specimen thickness, a is the crack length, K_c is the fracture toughness, W is the width of the specimen, and σ_y is the yield strength. It is clear from Figure 20 that a certain sample thickness is required in order to obtain a plane strain fracture behavior.

ASTM standard D5045 involves a three point bending (TPB) test on the syntactic foam core. ASTM Standard D 5045-99 is a standard test method designed to characterize the toughness of plastics in terms of the critical-stress-intensity factor, K_{Ic} , and the energy per unit area of crack surface or critical strain energy release rate, G_{Ic} , at fracture initiation. The material property K_{Ic} characterizes the resistance of a material to fracture in a neutral environment in the presence of a sharp crack under severe tensile constraint, such that the state of stress near the crack front approaches plane strain, and the crack-tip

Figure 20: Effect of specimen thickness on fracture toughness

plastic (or non-linear viscoelastic) region is small compared with the crack size and specimen dimensions in the constraint direction. A K_{Ic} value is believed to represent a lower limiting value of fracture toughness. This value may be used to estimate the relation between failure stress and defect size for a material in service wherein the conditions of high constraint described above would be expected measurement must be obtained to assure accuracy of the G_{Ic} value.

The standard assumes that the material behaves in a linear elastic way and a state of plane-strain at the crack tip is required which leads to specimens of sufficient thickness. The standard suggests the use of single-edge-notch bending (SENB) specimens, see

Figure 21: SENB specimen

Figure 38. Bakker [65] advised to keep the span-to-width ratio, S/W , at 4 in order to be able to use the existing equations for fracture mechanics [66]. Further, it is required that the specimens are notched and the crack must be sufficiently sharp to ensure that a minimum value of toughness is obtained.

Several strategies can be applied to improve the toughness of polymeric materials. The following paragraphs will discuss three different strategies and their related toughening mechanisms which might be relevant for the toughening of syntactic foams.

2.3.2 Rigid Particle Toughening

Numerous studies have shown that inorganic particles are able to toughen thermoset as well as thermoplastic polymers [67-75]. It should be understood that rigid particle toughening has some rather complicated aspects. Therefore, it seems improbable

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to derive a simple mechanism that is able to explain all the observed fracture behavior. Some of the toughening mechanisms, observed for rigid particle toughening are discussed in detail in the following subparagraphs.

a) Crack front bowing

According to [71], most publications consider the crack front bowing mechanism (or crack front pinning) as the major toughening mechanism for inorganic particle toughening. The crack front bowing mechanism was first proposed by Lange [76]. Lange used the ‘line tension concept’, developed in studies on dislocation motion in ceramic materials, to explain the toughening effect from the incorporation of rigid particles in brittle matrices. According to the crack front bowing mechanism, a crack, propagating through a matrix filled with rigid particles, is resisted by a rigid particle. The resistance of the rigid particle causes the crack to bend between particles, see Figure 22. The bowed secondary crack front has more elastic energy stored than the straight unbowed crack front. Due to the higher elastic energy stored in the bowed crack front, more energy is needed to propagate the crack. Lange derived a simple equation based on the line tension concept [76]:

$$G_c = 2 \left(G_m^0 + 2 \frac{T}{D_i} \right) \quad (2.2)$$

where G_c is the fracture energy of the composite, G_m^0 the fracture energy of the matrix, T the line energy per unit length of the crack, and D_i the inter-particle separation.

Figure 22 Crack Front Bowing Mechanism [77]

Figure 23 Tail structure [Wouterson et al., unpublished result]

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The bowed secondary crack front leave characteristic step structures or tails behind the particles, see Figure 23. The step structures represent a mismatch between two planes of crack propagation divided by a particle. The step structures are often regarded as evidence for the presence of the crack front bowing mechanism.

Over the years, Lange's crack front bowing mechanism has been modified by several researchers [78-81]. According to [71], as a whole, the crack front bowing theory is able to explain the crack propagation and the macroscopic fracture toughness of inhomogeneous materials though many experimental results, like i.e. the insignificant effect of surface treatment of inorganic particles, remain unexplained by using this mechanism

b) Debonding of glass beads/diffuse matrix shear (DS) yielding

Debonding of glass beads or microspheres occurs when a crack runs over the bead/matrix interface, exposing the bead/microspheres on one side of the fracture surface. An example of debonding is given in Figure 23 and Figure 24. Once the bead/microsphere debonds from the matrix, matrix shear yielding occurs around the surface region in a plane stress condition. The matrix shear yielding becomes visible under an optical microscope using crossed polarized filters, see Figure 25. The birefringent regions around the spheres indicate diffuse shear yielding. It is often observed that the birefringence is more intense around the equatorial regions. Although debonding of glass beads and diffuse matrix shear (DS) yielding are actually two different mechanisms, they are often combined due to their mutual occurrence.

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The opinions on the importance of debonding differ among researchers. Some researchers [82,83] consider the mechanisms involving debonding and matrix shear yielding as one of the most important toughening mechanisms as it triggers plastic deformation in the matrix which reduces the crack driving force. Others consider debonding as a minor toughening mechanism [70]. All researchers agree that quantification of the amount of energy dissipated through debonding and matrix shear yielding is hard to achieve. [71] attempted to correlate the size of the debonding zone and the fracture toughness but no reasonable correlation was obtained.

Figure 24: Debonded sphere [135]

Figure 25: Optical micrograph of glass bead debonding observed between crossed polarizers [63].

c) Micro-shear (MS) banding

In their work on glass bead reinforced polymers, Lee and Yee [43] discussed a third toughening mechanism present in particulate-reinforced polymers, namely micro-shear (MS) banding. An example of the MS banding as reported by [71] is shown in Figure 26.

According to [71], MS banding is thought to occur due to the strain softening behavior of materials and the existence of initial strain inhomogeneities. The critical strain to initiate MS banding, ϵ^c , can be calculated by a model proposed by Bowden [84]:

$$\varepsilon^c = \varepsilon^* \ln(\varepsilon^* / \Delta\varepsilon) \quad (2.2)$$

where ε^* is the characteristic strain of materials, and $\Delta\varepsilon$ is the initial strain inhomogeneity.

[71] reports that the inclusion of glass beads in epoxy systems can provide large $\Delta\varepsilon$ values and strain softening behavior of epoxies can provide favorable ε^* values for MS banding. The presence of glass beads in epoxy resins is likely to facilitate MS banding. MS bands initiate from the interface between glass beads and the matrix ahead of the crack tip, and then propagate through the matrix, absorbing a significant amount of energy.

Interestingly, it is reported by [71] that the occurrence of MS banding is matrix-dependent. MS banding was not observed in the more brittle matrices. Therefore, it can

Figure 26: Micro-shear banding

be expected that the MS banding mechanism is not a major toughening mechanism in more brittle matrix systems.

2.3.4 Fiber Toughened Polymers

Nowadays fiber reinforced plastics are used extensively in most segments of the transport industry. For example, cars [85], trains [86] and aircraft [87] all have increasing numbers of composite parts. Fiber composites are being used in the structures of these transport vehicles as fiber composites are able to exhibit as similar performance as conventional metal structures but at a reduced weight. The weight reduction compared to conventional metallic structures is not only caused by the lower density of the constituents of the composite but is also caused by the composites' ability to integrate functions. The fiber composites offer much more design freedom compared to conventional materials. For transport vehicles, weight is more and more becoming a dominant factor with the increasing fuel price and environmental issues. In addition, the tooling costs of are 50% lower compared to steel, the time-to-production is higher for fiber composites

Short-fiber-reinforced polymers (SFRP), see Figure 27, were developed to fill the mechanical property gap between the continuous-fiber laminates used as primary structures by the aircraft and aerospace industry and the un-reinforced polymers used in non-load-bearing applications. SFRP can be easily fabricated by the rapid, low-cost injection-molding processes. In the final products there exist continuous distributions of

Figure 27: Short-Fiber Reinforced Polymers [80]

fiber length and orientation which are governed by a variety of factors. These include the original length and concentration of fibers, the gate design and the processing conditions. The mechanical properties of SFRP have been studied by several researchers. The mechanical properties often can be estimated by means of a (modified) rule-of-mixtures [88].

The effect of the fiber length distribution (FLD) and the fiber orientation distribution (FOD) on the tensile and fracture properties have been addressed by several researchers [89-94]. For the fiber length, it is important to determine the so-called critical fiber length. The critical fiber length is defined as being a minimum fiber length required to build up the shear stress between fiber and resin to the value of tensile fracture stress

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of the fiber. Over or equal to this length, the maximum value of the load transfer from the matrix to the fiber can occur. If the fiber length is less than this length, the matrix can not effectively grip the fiber to take the strain and the fibers will slip and be pulled out, instead of being broken under tension. The composite will then exhibit lower mechanical performance.

Besides the length of the fibers, the orientation of the fibers also plays an important in the overall properties of the composite [92,151]. Depending on the orientation of the fibers can be categorized according to the following fiber orientations: unidirectional, random, partially aligned. [151] show that the Young's modulus reduces for randomly and partially aligned fibers, see Figure 28. The highest modulus was observed for unidirectional fibers. It was also observed that the drop in the modulus with increasing fiber angle was greater for higher fiber content.

Inclusion of fibers in a polymer matrix has proven to be an effective method to increase the toughness of the composites, including thermoset and thermoplastic matrices [95-101]. Toughening is often based on the so-called fiber-bridging effect, see Figure 29. According to Harris [102], in the uncracked composite, see Figure 29a, the fiber is gripped by the matrix. A matrix crack is halted by the fiber, see Figure 29b. Increasing the load allows the crack to pass around the fiber without breaking the interfacial bond. Interfacial shearing and lateral contraction of the fiber result in debonding and a further increment of crack extension, see FigureFigure 29c. Figure 29d and Figure 29e show that after considerable debonding the fiber breaks at some weak spot within the matrix and

Figure 28: Composite Elastic modulus as a function of the mean fiber orientation

Figure 29: Model of crack-fiber interactions in a simple composite [153]

further crack extension occurs. The broken fiber end must be pulled out against the frictional grip of the matrix if total separation of the composite is to occur.

2.3.5 Nano Toughened Polymers

In recent years, it has been proven by many researchers that nanoparticles are able to toughen polymeric materials [103,104]. The improved properties of nanoparticle-filled polymer composites are attributed to the exceptionally large interfacial area in the composites. The interface between the nanoparticles and the polymer matrix controls the degree of interaction between the filler and the polymer and thus controls the properties.

A: Conventional Composite

B: Intercalated Nanocomposite

C: Ordered Exfoliated Nanocomposite

D: Disordered Exfoliated Nanocomposite

Figure 30: Schematic illustrations of (A) a conventional; (B) an intercalated; (C) an ordered exfoliated; and (D) a disordered exfoliated polymer–clay nanocomposites [105].

Figure 31: TEM image of an aggregate of intercalated clay [162]

Figure 32: TEM image of exfoliated clay layers [162]

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In particular, polymer based nanocomposites reinforced with montmorillonite particles have drawn significant attention [105-125]. These types of nanocomposites have shown substantial improvements in mechanical, thermal and barrier properties over the pristine polymer, and therefore, have potential in high-performance applications.

In general, two polymer idealized polymer layered silicate structures are possible: intercalated and exfoliated. In intercalated nanocomposites, the insertion of polymer into the clay structure occurs in a crystallographically regular fashion and typically few molecular layers occupy the gallery region. On the other hand, in exfoliated nanocomposites, the individual clay layers are dispersed in a continuous polymer matrix and segregated from one another by average distances that depend on the clay loading.

In their work, Wang et al. [162] give a nice overview of the different views that researchers have on the toughening effect of nanoclay layers. Zilg et al. [113] suggested that an exfoliated structure mainly leads to an improved modulus, while the remaining stacked structure of intercalated clay platelets is the key to improve toughness. Zerda et al. [124] proposed that the creation of additional surface area on crack propagation was the primary toughening mechanism. Kornmann et al. [125] and Kinloch et al. [103] also noticed that the fracture toughness of the epoxy/clay nanocomposite is lower than that of microcomposites. It was suggested that the toughening effect is due to crack deflection and plastic deformation initiated around the particles, which leads to the formation of cavities. In addition it was suggested that the clay could have been swollen, leading to a large size but low aspect ratio. Wang et al. [162] concluded that the formation of a large

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number of microcracks and the increase of fracture surface area due to crack deflection are the major toughening mechanisms in the epoxy/clay nanocomposite.

Although the high aspect ratio of silicate nanolayers is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics. For this reason, many researchers make use of so-called modified nanoclay whereby the surface chemistry of the clay and the hydrophobic polymer matrix has been compatibilized. Besides modification of the clay, processing parameters play a role in the dispersion of the clay. Different processing techniques can be employed to disperse the nanoclay particles in the polymer matrix. Some of the techniques include in-situ polymerization, high speed shear mixing, ultrasonification. For Zunjarrao et al. [118] the best improvements were observed for high speed shear mixing.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Materials

3.1.1 Matrix

A syntactic foam is a ternary material comprising of two components, namely a matrix (binder) and hollow spheres (filler). All the test results discussed in this thesis report are based on samples having an epoxy resin as the binder. The epoxy resin used was Epicote 1006, supplied by Wee Tee Tong Chemicals Pte. Ltd. Epicote 1006 is combination of liquid bisphenol-A, epichlorohydrin epoxide resin, amine and polymeric additives. The Epicote 1006 epoxy system comprises of a pure resin (epoxy pre-polymer) and a hardener (curing agent). The hardener is required to form a network of chemical bonds among the molecules of the prepolymer. This process of building up the network of chemical bonds is called 'curing process'. Table 3.1 shows some of the properties of the epoxy resin as given by the supplier.

*Experimental Details***Table 3.1: Properties of Epicote 1006**

Specific Gravity (-)	1.11
Compressive Strength (MPa)	81.86
Tensile Strength (MPa)	29.81
Flexural Strength (MPa)	74.24
Tensile Shear Strength (MPa)	4.22
Elongation (-)	1.9%
Mixing Ratio Resin : Hardener (wt%)	5:3

3.1.2 Microspheres

The filler used to create the porosity in syntactic foam comprised of hollow microspheres. Three different types of microspheres were used, namely hollow glass microspheres, 3M™ Scotchlite Glass Bubbles K15 and K46 and Phenoset BJO-093 hollow phenolic microspheres, supplied by Asia-Pacific. Properties of the various microspheres can be found in Table 3.2 and 3.3. Figure 33 shows an SEM image of hollow glass microspheres.

According to 3M [126], Scotchlite glass bubbles are made of soda-lime-borosilicate glass. The chemically-stable soda-lime-borosilicate glass composition of Scotchlite glass bubbles provides excellent water resistance. The low alkalinity of

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Table 3.2: Properties of different microspheres

Microsphere	Density	Static Pressure	Mean Diameter	Wall Thickness
	[g/cm ³]	[MPa]	[μm]	[μm]
BJO-093	0.25	3.44	71.5	1.84 ⁺
K15	0.15	2.07	70 [*]	0.70
K46	0.46	41.37	43.6	1.37

* from Bardella et al. [41],

+ from SEM measurement

Table 3.3: Particle Size of 3M Scotchlite Glass Bubbles

Microsphere	Particle Size (microns, by volume)			Effective Top Size (microns)
	Distribution			
	10 th %	50 th %	90 th %	
K15	30	60	105	115
K46	15	40	70	80

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Figure 33: SEM image of K15 microspheres

Scotchlite glass bubbles makes them compatible with most resins, featuring a stable viscosity and long shelf life. The unique spherical shape of Scotchlite glass bubbles offers a number of important benefits, including: higher filler loading, lower viscosity/improved flow and reduced shrinkage and warpage.

3.2 Processing of Syntactic Foam

The main challenge in processing a syntactic foam lies in the choice of the process parameters (temperature, mixing time, and addition sequence) for mixing the components. When the mixture leaves the mixing beaker, the viscosity must be low enough for the mold to be filled rapidly, and once the mold is filled up, the viscosity should rise rapidly to prevent lamination of the mixture.

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For the work presented in this thesis, an epoxy resin, see paragraph 3.1.1, was used. The epoxy system comprised of an epoxy prepolymer and a hardener. Both components had a liquid appearance at room temperature. Based on the mixing ratio between the prepolymer and the hardener, a stoichiometric amount of hardener is added to the prepolymer. A glass rod is then used to mix the two components thoroughly. Mixing the two components, created chemical bonds among the molecules of the epoxy prepolymer and hardener. This process of creating bonds is called the curing process. The curing process of epoxy resin is an exothermic process. The obtained mixture had to be stirred by hand for a couple of minutes until the filaments visible with the naked eye, due to the contact of the hardener and epoxy component, were no longer visible. Stirring was performed cautiously to avoid the formation of air bubbles.

Based on the preferred microstructure, a specific amount of microspheres was added to the epoxy resin. The amount of microspheres was added in small portions to avoid the formation of resin necking. Resin necking occurs when a group of microspheres is trapped inside the resin, affecting the mechanical and fracture properties of syntactic foam. Once thoroughly mixed, the mixture was poured into an aluminum mold which was pre-treated with a silicone layer allowing easy removal of the syntactic foam after curing. The filled mold was put under a press and left overnight to allow the syntactic foam to cure under room temperature conditions. Once the syntactic foam was cured, it was taken out of the mold and it was ready for cutting the desired shapes.

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Figure 34: Cold Isostatic Press

3.3 Mechanical Testing

3.3.1 Tensile Tests

For the tensile tests, syntactic foam was machined into rectangular shapes of 170 mm × 18 mm × 6 mm. The specimens were cut in the specific size to facilitate the use of a ‘dogbone’ template available in MSE. A TensilKut I machine, supplied by TensilKut Engineering, was used to cut each specimen into a ‘dog-bone’ specimen. The dimensions of the resulting tensile specimens were similar to the dimensions of Type 1 specimens shown in ASTM Standard D-638-01 [127], see Figure 35.

The tensile tests were carried out at room temperature using an Instron Testing Machine (Model 5567) at a crosshead speed of 5.0 mm/min. For each test the strain was

Specimen Dimensions for Thickness, T , mm (in.)^a

Dimensions (see drawings)	7 (0.28) or under		Over 7 to 14 (0.28 to 0.55), incl		4 (0.16) or under		Tolerances
	Type I	Type II	Type III	Type IV ^b	Type V ^{c,d}	Type VI ^e	
W —Width of narrow section ^{E,F}	13 (0.50)	6 (0.25)	19 (0.75)	6 (0.25)	3.18 (0.125)	3.18 (0.125)	$\pm 0.5 (\pm 0.02)^{E,C}$
L —Length of narrow section	57 (2.25)	57 (2.25)	57 (2.25)	33 (1.30)	9.53 (0.375)	9.53 (0.375)	$\pm 0.5 (\pm 0.02)^C$
WO —Width overall, min ^a	19 (0.75)	19 (0.75)	29 (1.13)	19 (0.75)	...	...	+ 6.4 (+ 0.25)
WO —Width overall, min ^a	...	...	...	...	9.53 (0.375)	9.53 (0.375)	+ 3.18 (+ 0.125)
LO —Length overall, min ^H	165 (6.5)	183 (7.2)	246 (9.7)	115 (4.5)	63.5 (2.5)	63.5 (2.5)	no max (no max)
G —Gage length ^I	50 (2.00)	50 (2.00)	50 (2.00)	...	7.62 (0.300)	7.62 (0.300)	$\pm 0.25 (\pm 0.010)^C$
G —Gage length ^I	...	...	...	25 (1.00)	...	...	$\pm 0.13 (\pm 0.005)$
D —Distance between grips	115 (4.5)	135 (5.3)	115 (4.5)	65 (2.5) ^J	25.4 (1.0)	25.4 (1.0)	$\pm 5 (\pm 0.2)$
R —Radius of fillet	76 (3.00)	76 (3.00)	76 (3.00)	14 (0.56)	12.7 (0.5)	12.7 (0.5)	$\pm 1 (\pm 0.04)^C$
RO —Outer radius (Type IV)	...	...	...	25 (1.00)	...	...	$\pm 1 (\pm 0.04)$

Figure 35: Tensile specimen dimensions

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Figure 36: Setup for tensile testing of syntactic foam

Figure 37: Syntactic foam specimens for flatwise compression test; (a) after testing, (b) before testing.

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recorded with a clip-on strain gauge, see Figure 36. The Young's modulus, E_t , was measured from the initial region of deformation.

3.3.2 Compression Tests

For the flatwise compression test, syntactic foam was machined to blocks of 25 mm × 25 mm × 12 mm, see Figure 37. The length and width were chosen according to ASTM C365-00 [128] as the syntactic foam is most likely to be used as the core material in sandwich composites. The height of the specimen was chosen based on the studies performed by Gupta [22]. Low aspect ratio specimens were used to minimize the effect of the shear stress. The tests were carried out at room temperature using an Instron Model 4206 with a maximum capacity of 100 kN. The crosshead speed was 0.5 mm/min. The flatwise compressive yield strength of syntactic foam was calculated by [128]:

$$\sigma_c = \frac{P_y}{A} \quad (3.1),$$

where σ_c is the compressive yield strength, P_y the load at yield, and A the cross-sectional area.

The flatwise compression modulus, E_c , was calculated by [128]:

$$E_c = \frac{mt}{A} \quad (3.2),$$

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where m is the slope of the initial linear region of the load-deflection curve, A is the cross-sectional area, and t the thickness of the syntactic foam.

3.3.3 Flexure Tests

For the flexural tests, syntactic foam was machined to specimens of 127 mm × 12.7 mm × 3 mm in dimensions. The tests were performed by an Instron 5567. The span of the support, S , was chosen to be 48 mm in order to achieve a span-to-depth ratio of 16 as recommended by the ASTM D790-00 [52]. The strain rate was maintained at 0.01 min⁻¹. The crosshead speed, z , was calculated by [52]:

$$z = \frac{R * S^2}{6t} \quad (3.3),$$

where R is the strain rate, and S the span of the support.

The bending modulus, E_b , was calculated by [52]:

$$E_b = \frac{S^3 m}{4Wt^3} \quad (3.4),$$

where S is the span of the support, and W is the width of the testing sample.

3.3.4 Fracture Toughness Testing

In the fracture toughness assessment under quasi-static loading, single-edge notched bend (SENB) specimens, see Figure 38, were loaded in a three-point bend (3PB) geometry, see Figure 39. The tests were performed by an Instron 5567 at a crosshead speed of 5 mm/min. The specimen dimensions were 60 mm × 12.7 mm × 6.35 mm. For all the specimens, a constant crack-to-width ratio, a/W , of 0.5 was prepared by a vertical band saw. A sharp crack was introduced by tapping a fresh razor blade into a notch.

The critical stress intensity factor, K_{Ic} , can be estimated from the following equations [73]:

$$K_{Ic} = Y \frac{3PS\sqrt{a}}{2tW^2} \quad (3.5),$$

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.80\left(\frac{a}{W}\right)^4 \quad (3.6),$$

where Y is a shape factor, P is the peak load at the onset of crack growth in a linear elastic fracture, W the width of the specimen, S the support span, and a the crack length. Based on a span-to-width ratio, S/W , equal to 4, the coefficients, in Equation 3.6, were obtained from Brown and Srawley [66].

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Figure 38: Appearance of syntactic foam SENB samples after compression molding and machining.

Figure 39: Test setup of three-point bending test of SENB specimens.

3.3.5 Impact Testing

In the impact resistance assessment, SENB specimens of the dimensions of 127 mm $\times$ 12.7 mm $\times$ 6.35 mm were prepared. The specimens were notched to $a/W = 0.25$ by using a vertical band saw. A sharp crack was introduced by tapping a fresh razor blade into a notch. The specimens were tested on a Ceast Resil Impactor with an instrumented hammer at a velocity of 3.46 m/s.

Compared to non-instrumented pendulums, the use of instrumented pendulums simplifies the test. An instrumented pendulum has a strain gauge at the tub of the striker. A strain gauge is made of piezo-electric material which means that there is a coupling between an electric signal and a mechanical load/strain. During the impact, the strain gauge is deformed by the impact loading. This deformation will result in an electric signal that can be processed inside a data processor. This data processor can acquire 1000 data points in a millisecond.

The main property that can be obtained from the Charpy impact test is the impact resistance. The impact resistance indicates the energy that is required to fracture a unit area of material. How the energy, that is necessary to fracture a specimen in a Charpy impact test, can be calculated is clearly stated by Fernández-Canteli et al. [129]. According to Fernández-Canteli et al. the deformation can be expressed as:

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$$x(t) = \int_0^t v_0 - \left(\frac{1}{m} \right) \int_0^t F(y) dy \quad (3.7),$$

or

$$F(x) = \frac{d}{dy} \left[m \left(v_0 - \frac{dx(y)}{dt} \right) \right] \quad (3.8),$$

where x = deflection of the specimen at the impact point
 v_0 = initial impact velocity of the pendulum
 F = registered force
 y = time elapsing from the beginning of loading

The work can now be calculated by integrating equation 3.8 over the total deformation during the impact. The work that is obtained is then equal to the energy necessary for impact:

$$Energy = \int_0^x F(x) dx \quad (3.9).$$

3.4 Microscopy

3.4.1 Scanning Electron Microscopy (SEM)

To study the fracture behavior of syntactic foam that had been mechanically tested, the fracture surface was cut from the specimen with a vertical band saw. A layer of gold was coated onto the fracture surface by means of a gold coater (SPI module). The

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mechanical and fracture behavior of syntactic foam was then characterized by means of a Jeol JSM 5410LV, low vacuum scanning electron microscope (SEM).

3.4.2 Optical Microscopy (OM)

To study the deformation zone ahead of sub critically loaded crack tip, a petrographic thin sectioning technique was adopted [130]. An optical microscope (Nikon Eclipse E600 POL) was used to study the sub-surface damage in the process zone of a 3PB specimen. The center section, containing the initiated crack was cut from the SENB specimen using a vertical band saw, followed by encapsulation in epoxy resin. To facilitate the study, the sample was polished through the mid-section using a Struers Rotapol-35 polisher. Grinding and polishing were performed using silicon carbide polishing papers with grade numbers from 320, 500, 800, 1200 to 4000, respectively, followed by diamond paste containing particles of 3 μm and 1 μm in sizes. Thin-sections were taken from the specimen's mid-plane, perpendicular to the fracture surface by means of a Buehler Petro-thin Thin Sectioning System. The thin section was observed under a transmission optical microscope with bright and polarized light.

3.5 Thermal Analysis

3.5.1 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis measures the force and deflection of the specimen while varying the temperature and/or frequency. The instrument calculates the storage

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modulus, loss modulus and damping coefficient as a function of temperature. The glass transition temperature can be determined from the resulting curves.

Dynamic mechanical analysis was performed using a TA DMA 2980 equipped with TA thermal analysis software. Syntactic foam was machined to rectangular pieces of 55 mm × 15 mm × 6 mm. The specimens were tested in a three point bending configuration from room temperature to 110 °C at a scan of 5 °C/min at a frequency of 1 Hz.

3.5.2 Thermogravimetric Analysis

A high resolution TGA 2950 Thermogravimetric Analyzer (TGA) equipped with TA thermal analysis software was used to study the thermal stability of syntactic foam. The specimens, a few mg in weight, were heated from room temperature to 800°C at 20°C/min in a nitrogen environment.

CHAPTER 4

EFFECT OF POROSITY ON THE MECHANICAL, THERMAL AND FRACTURE PROPERTIES

4.1 Introduction

Using hollow particles, having a density lower than the binder material, allows for the manufacturing of light-weight materials with the increasing filler content. In this sense, syntactic foam differentiates itself from the general particulate-filled polymer composite (PFPC), whose density increases with increasing filler content. The mechanical and fracture behaviors of the PFPC have been studied extensively [131]. The moduli and fracture properties often improve with increased solid filler content, given an intrinsically brittle matrix system and good interfacial bonding between the filler and the matrix.

Most studies on the mechanical and fracture properties of syntactic foams are based on the maximum filler content of microspheres as this elicits the lowest possible weight of the composites [22,24,53]. In this Chapter, the influence of different compositions of syntactic foam on its specific mechanical and fracture properties is investigated. A comprehensive understanding of the structure–property relationship is

Effect of Porosity

lacking. Different compositions will be created by varying the type and volume fraction of microspheres. This route is different from that reported by Gupta et al. [27] whereby different microstructures were created by using different types of microspheres with similar size distributions while keeping the volume fraction of microspheres constant for each type of microspheres.

It is essential that specific properties be discussed in this chapter because the density of syntactic foam changes with the amount of microspheres introduced. Specific properties allow for the comparison of the performance of syntactic foams to other potential foam materials in sandwich composites such as PU, PVC and aluminum foams. Furthermore, specific properties aid the comparison between the different microspheres used in this study. By normalizing mechanical and fracture properties against the density, it is believed the results would be fruitful for guiding future design for syntactic foams based on specific properties. Results from tension, compression, flexure and fracture tests will be discussed in relation to their microstructures.

4.2 Density vs. Microsphere Content

The syntactic foam was manufactured according to the processing conditions described in paragraph 3.2. A general microstructure of syntactic foam is shown in Figure 40. Provided the density of the hollow microsphere is lower compared to the density of the binder, inclusion of hollow microspheres in syntactic foam leads to a reduction in the

Effect of Porosity

Figure 40: General structure of syntactic foam

Figure 41: Density variation with microsphere content for syntactic foam containing various types of microspheres; (■) K15, (▲) K46 and (●) Phenolic microspheres.

Effect of Porosity

density of the syntactic foam. Figure 41 shows the measured densities of syntactic foams with increasing hollow microsphere content for the three different types of microspheres, discussed in paragraph 3.1.2. The measured densities presented in Figure 41 are an average of 30 samples. For each sample, the length, width, thickness and weight was recorded. The density was calculated by dividing the volume of a specimen by its weight. Figure 41 shows, that all three types of microspheres show a linear decreasing trend in the density with increasing filler content. The linear trend is expected from the rule of mixtures. The theoretical density of each composition is calculated according to the rule of mixtures. It is clear that the measured density of syntactic foam is lower compared to the theoretical density. The lower value in density is caused by the presence of voids in the composite which are created during mechanical mixing of the components of syntactic foam. The voids will affect the mechanical properties. The void content for the different microstructures has been estimated by the following equation according to ASTM D-2734 [132]:

$$V_v = 100 \times \frac{(\rho_{theoretical} - \rho_{measured})}{\rho_{theoretical}} \quad (4.1),$$

where V_v is the void volume fraction, $\rho_{theoretical}$ is the theoretical density, and $\rho_{measured}$ is the measured density. The void volume fraction is provided in Table 4.1.

Table 4.1: Mechanical properties and void content of studied compositions of syntactic foam

	Tensile Strength [MPa]	Young's Modulus [GPa]	Yield Strength [MPa]	Compression Modulus [GPa]	Flexure strength [MPa]	Flexure Modulus [GPa]	Fracture Toughness [MPa.m ^{1/2}]	Void % [-]
Epoxy	29.81	2.68	85.54	1.04	78.61	2.82	0.83	2.91
10% K15	37.32	2.76	52.95	0.88	56.61	2.31	0.95	5.14
20% K15	32.95	2.55	54.18	0.68	43.63	2.07	1.20	6.86
30% K15	23.68	2.23	44.73	0.66	27.67	1.81	1.16	9.18
40% K15	18.96	2.07	37.96	0.63	25.59	2.06	0.94	8.85
50% K15	17.45	1.99	31.17	0.63	22.51	1.99	0.71	7.02
10% K46	43.29	2.82	84.61	0.95	53.32	2.97	1.17	4.87
20% K46	32.87	3.12	80.64	1.14	36.04	3.13	1.39	6.07
30% K46	26.21	3.29	76.63	1.14	31.38	3.22	1.27	8.44
40% K46	23.25	3.41	NA	NA	33.39	3.58	0.95	10.21
50% K46	23.23	3.78	NA	NA	33.99	3.86	NA	10.02
10% BJO	40.84	2.39	62.87	0.80	60.47	2.14	0.87	3.95
20% BJO	32.16	1.88	51.08	0.71	46.70	1.90	0.99	3.69
30% BJO	25.75	1.58	38.11	0.63	38.91	1.52	1.15	8.76
40% BJO	22.29	1.33	31.39	0.57	31.52	1.25	0.92	8.61
50% BJO	15.50	1.17	25.95	0.53	27.22	1.09	0.66	8.03

4.2 Mechanical Properties

4.2.1 Tensile properties

Syntactic foam behaves like a linear-elastic material up to failure when loaded in tension. The material experiences catastrophic failure across a plane perpendicular to the tensile axis, see Figure 42. Luxmoore and Owen [39] concluded that a crack will initiate from an oversized void when a composite is subjected to tensile loading. Indeed, numerous specimens fractured at a cross-section containing a void. The specific tensile strength, σ_t/ρ , for various compositions of syntactic foam are shown in Figure 43a. The results are based on an average of 5 tests. The error bar is the standard deviation for five measured values. The trends in the tensile strength, σ_t , with increasing microsphere

Figure 42: Syntactic foam specimens after being subjected to tensile loading.

Effect of Porosity

content are rather similar for the three types of microspheres, except for 50 vol% phenolic microspheres. Figure 43a shows that σ_t/ρ increases upon inclusion of a small amount of microspheres when compared to neat epoxy resin. The presented data for neat epoxy are obtained experimentally. However, beyond 10 vol%, a decreasing trend in σ_t/ρ is observed for all types of microspheres. The decreasing trend in σ_t/ρ with increasing filler content indicates that the relative reduction in strength is larger than the relative reduction in density. Indeed, a decrease in σ_t with increasing filler content is observed, see Table 4.1. The comparable trends and values suggest that σ_t/ρ is independent of the microsphere type and size, but only varies with the microsphere volume fraction. The following curve-fitting relation between the σ_t/ρ and the volume fraction of microspheres, x , has been derived for $0.1 < x < 0.5$:

$$\frac{\sigma_t}{\rho} = -2157x^4 + 2712x^3 - 1050x^2 + 93x + 40.768 \quad (4.2)$$

Luxmoore and Owen suggested [39] that the failure of the foam is attributed to the failure of the resin matrix. The non-linearity in σ_t/ρ is caused by the reduction in the area of the epoxy matrix in a cross-sectional area. Introduction of hollow microspheres reduces the epoxy volume fraction and increases the inhomogeneity content, consequently reducing the tensile strength of the composite as a result of poor interfacial strength between the matrix and the filler. The author assumes that the matrix serves as the load-bearing phase in the composite whereas the hollow microspheres only

Effect of Porosity

(a)

(b)

Figure 43: Specific tensile properties of syntactic foam containing various microspheres; (a) Specific tensile strength, and (b) Specific Young' s modulus.

Effect of Porosity

provide light weight and minimal strengthening effect. The reduction in load-bearing volume outweighs the increase in stiff microsphere shells. Around 40 vol% of filler content, a minimum is observed for all the microspheres. The author believes that 40 vol% of microspheres is to be the maximum amount of filler which can be fully wetted by the epoxy matrix in this system. The change in properties and behavior of syntactic foam around 40 vol% was also observed by Bunn and Mottram [32]. Nevertheless, clear advantages regarding other mechanical properties arise upon introduction of hollow microsphere as shown in the discussion that follows.

It has been reported that the Young's modulus, E_t , generally decreases with increasing content of hollow microspheres [42,43]. So far only Bardella and Genna [41] report an increasing trend in E_t for syntactic foams containing K37 ($\rho = 0.37 \text{ g/cm}^3$) microspheres. The results from the current research, as presented in Figure 43b shows similarity to those in [41] in the sense that the trend for the specific Young's modulus, E_t/ρ , with increasing filler content depends on the type of microspheres used. K46 microspheres show a rather linear increase in E_t/ρ , whereas K15 show a constant trend. Based on the data presented in Table 4.1, it is known that the constant trend in E_t/ρ is caused by a proportionate decrease in the Young's modulus and the density. For hollow phenolic microspheres, a decrease in E_t with increasing microspheres content is observed. The value obtained for neat epoxy resin is too low considering the trends in E_t for syntactic foams containing the three different types of microspheres. The lower value for neat epoxy resin could be caused by the presence of voids, see Figure 44. The differences

Figure 44: Oversized void at the fracture surface of syntactic foam

between the results for K46 and K15 microspheres can be attributed to their size and wall thickness. It has been shown by several researchers that, in general, for microspheres of the same material composition, improved mechanical properties are obtained for the microspheres with a higher density. Higher density for microspheres of the same material is often associated with a larger thickness-to-radius ratio, t/R , see Table 3.2. Syntactic foam containing microspheres of the same material having a larger t/R often exhibit improved mechanical properties [133]. The difference between the phenolic and K15 glass microspheres explains that apart from microsphere size, the material composition of the microsphere is of equal importance for the mechanical properties. Phenol-formaldehyde has an E_t of about 6.8 GPa whereas soda lime glass has an E_t of about 77 GPa. The difference in E_t is believed to be an important factor to the difference in the trends of hollow glass and phenolic microspheres. This relationship between the material

Effect of Porosity

of the matrix and the inclusion was studied by Pawlak and Galeski [134]. It was found that the higher the Young's modulus of the inclusion compared to the epoxy used, the higher the stresses developed in the material. Further they observed that the position of the maximum stress at the spherical inclusion changed from the pole for hard inclusion to the equator for soft inclusion.

Figure 45 shows an SEM fractograph of a tensile specimen; the micrograph confirms the role of the binder in the failure of syntactic foam under tensile loading. The micrograph shows a rough surface of the epoxy resin after brittle fracture. Numerous step structures can be identified in Figure 45 which indicates the plastic yielding of the epoxy

Figure 45: Fracture surface of syntactic foam perpendicular to the direction of applied tensile loading.

Effect of Porosity

resin. Besides plastic yielding, intact microspheres are observed on the fracture surface. The fact that the crack has grown over the interface between the matrix and the microsphere indicates the presence of debonding. Debonding of hard inclusions was also reported by Pawlak and Galeski [134]. The debonding is caused by the complex stress state around the particle–matrix interface which will not be further discussed here.

4.2.2 Compression properties

Figure 46 shows the stress–strain curves of flatwise compression tests of syntactic foams containing various amounts of K15 microspheres (0-50 vol%). The compression

Figure 46: Compression curves of syntactic foam with various amounts of K15 microspheres content. Regions I-III are sequentially observed and indicated.

Effect of Porosity

curves of syntactic foam were previously discussed by other investigators [22,24,32]. For each individual curve, three different regions can be identified in Figure 46. The first region (I) is characterized by an almost linear-elastic behavior of the syntactic foam. The region ends when the material starts to yield and reaches its compressive yield strength. Upon yielding, the microspheres become crushed under the compression load and severe damage occurs. Yielding and inelastic damage occur during the test as the sides of the specimen barrel outward under compression loading, see Figure 37. Barreling of the specimen is caused by friction between the contact surfaces. It affects the stress of the syntactic foam under loading. The second region (II) of the flatwise compression curves in Figure 46 is characterized by relatively horizontal plateaus. The horizontal plateau is attributed to the implosion of the hollow microspheres under the increasing compression load. Syntactic foams with higher fractions of hollow microspheres show a larger horizontal plateau and thus a larger strain. The third region (III) is characterized by a steep increase in the load–displacement curve. The steep increase is caused by a large number of microspheres being crushed and compacted, and the maximum density is being reached. The point, where region III starts, is considered to be point of failure for the syntactic foam as this is the point where most of the load-bearing microspheres have been crushed.

The overall results of the flatwise compression tests are given in Figure 47a and b and the void content is summarized in Table 4.1. Figure 47a shows that the specific compressive yield strength, σ_{yc}/ρ , decreases with increasing filler content for phenolic and K15 microspheres. The microspheres act as voids and weaken the structure.

Effect of Porosity

(a)

(b)

Figure 47: Specific compressive properties of syntactic foam containing various microspheres; (a) Specific compressive yield strength, and (b) Specific compressive modulus.

Effect of Porosity

Nevertheless, an upward trend in σ_{yc}/ρ is observed for K46 microspheres. The upward trend is attributed to a relatively minor decrease in the compressive yield strength, see Table 4.1, compared to the relatively larger decrease in density. From the difference in trends between the K15 and K46 microspheres, it is induced that σ_{yc}/ρ is influenced by the wall thickness of microspheres.

The results for the specific compressive modulus, E_c/ρ , are shown in Figure 47b. Again K46 microspheres perform better as shown. The performance of K46 microspheres is also attributed to their $\frac{t}{r}$ ratio. For all microspheres investigated, it appears a densification process takes place at low filler content (~ 10 vol%). The densification is caused by a compaction process of the matrix polymer in the presence of voids in curing.

Figure 48: SEM micrograph of syntactic foam in region II of the compression strength vs. strain curve. The black arrows indicate the direction of compression.

Effect of Porosity

As the microsphere content increases and matrix volume decreases, the microsphere takes up more load under compression and, as a result, the specific compressive moduli increase. The trend under compression is in contrast to that under tension. K15 and phenolic microspheres show a rather similar behavior in E_c/ρ . Both show a minimum around 20 vol%, after which the E_c/ρ slightly increases. This increase is higher for K15 microspheres. The specific compressive stiffness levels off as the increase in stiffness is counter-balanced by the increases in density of the composite.

Figure 48 shows an SEM micrograph of the mid-section of a specimen which has been loaded beyond the compression yield strength. Clearly, the failure mode is crushing of the microspheres under the applied compressive load and compaction of the matrix and microspheres simultaneously. The elliptical voids indicate that the microspheres have been crushed under compression loading and the remaining pore has been deformed to an elliptical shape. Intact microspheres and sphere-shaped voids can also be seen, indicating that the syntactic foam has not reached its maximum compression strain but is still in the horizontal plateau of the load vs. displacement curve, see Figure 46.

4.2.3 Flexural properties

Figure 49a and Figure 49b show typical stress–strain curves for syntactic foams containing K46 and BJO-093 microspheres, respectively. The flexure behavior of K15 microspheres is not shown as it is similar to the flexure behavior of BJO-093 microspheres. For all specimens, it is observed that the strain is reduced with increasing filler content. Especially, the syntactic foams containing K46 microspheres show a larger

Effect of Porosity

(a)

(b)

Figure 49: Flexure stress strain curves of syntactic foam containing various amounts of (a) K46 and (b) phenolic microspheres. The arrow indicates the direction of increasing filler content.

Effect of Porosity

Figure 50: A deformed hollow phenolic microsphere

reduction in failure strain. The larger reduction in strain for K46 microspheres is attributed to the higher strength of the K46 microspheres, see Table 3.2. Fewer microspheres will fracture under the applied load which prevents stress relief in the material. On the contrary BJO-093 and K15 microspheres fracture more easily, relieving the stress in the material, and thus showing a larger strain.

Upon fracture some plastic deformation is observed for most compositions of syntactic foam with up to 30 vol% of microspheres. The amount of plastic deformation decreases with increasing filler content since the plastic deformation is attributed to the behavior of the epoxy binder. Syntactic foams containing hollow phenolic microspheres show larger plastic deformation compared to K46 and K15 microspheres. The latter might be attributed to ductile deformation of hollow phenolic microspheres as

Effect of Porosity

shown in Figure 50; an observation that has not been seen for hollow glass microspheres. The plastic deformation of syntactic foam containing hollow phenolic microspheres can be clearly seen on the fracture surface of specimens due to stress whitening. The stress whitening cannot be distinguished on syntactic foam containing hollow glass microspheres since the resulting syntactic foam is white in color.

During flexure loading, the specimen is subjected to compressive stresses on the top part of the specimen and to tensile stresses at the lower part of the specimen. From the tension and compression data presented in the previous paragraphs, it is expected that syntactic foam subjected to flexure loading will fail at the side under tensile stresses. Indeed, failure at the lower specimen side under tensile stresses is observed during experimental work. All specimens fail at the center of the support span. No indentation of the indenter is observed. The comparable failure mode under tensile loading and three-point-bending explains why there is some resemblance between Figure 43 and Figure 51. The only difference observed is the behavior of syntactic foams with 0–10 vol% of microspheres.

For the specific flexural strength, σ_f/ρ , see Figure 51a, some differences between the different compositions are observed. The differences are mainly caused by the difference in density between the different compositions as the values and trends are rather similar for the maximum flexural strengths, see Table 4.1. All types of microspheres show a decreasing trend in the maximum specific flexural strength with increasing filler content. Similar to the tensile test results, the specific strength

Effect of Porosity

(a)

(b)

Figure 51: Specific flexural properties of syntactic foam containing various microspheres; (a) Specific flexure strength, and (b) Specific flexure modulus.

Effect of Porosity

approaches a minimum around 40–50 vol% of filler content. Based on the data presented in Table 4.1, it can be said that the horizontal trend for the hollow phenolic and K15 microspheres at high volume fractions, is caused by a proportionate decrease in the flexure strength and density.

The trends and values in the specific flexural modulus, E_f/ρ , see Figure 51b, are consistent with the results presented in Figure 43b. The similarity is again attributed to the tensile failure mode of syntactic foam under three point bending. The K46 microspheres show an increase in E_f/ρ with increasing filler content. K15 microspheres show a constant value for E_f/ρ whereas phenolic microspheres show a decrease with increasing filler content. The constant value in E_f/ρ from K15 microspheres is attributed to a similar relative decrease in the flexure modulus and density, see Table 4.1.

SEM fractographs of the specimens tested under three point bending, see Figure 52, reveal the different loading modes at the upper and lower parts of the cross-sectional area of the specimen. Figure 52a shows the fracture surface of the lower part of the cross-section, which is loaded in tension. The fractograph is consistent with that in Figure 45. The surface is characterized by a rough surface. In between the tension and compression sides of the specimen, an area with relative smooth features is observed. The transition between the tensile surface and the compressive surface is shown in the right side of Figure 52b. The compressive surface shows step structures behind the microspheres. The step structures diminish with increasing filler content and are less pronounced for phenolic microspheres. Besides the step structures, debonded microspheres can be

Effect of Porosity

identified. Debonded microspheres indicate a poor interface between the matrix and the filler.

4.3 Fracture Properties

4.3.1 Effect of microspheres on the fracture toughness

Figure 53 and Figure 54 show the specific fracture toughness, K_{Ic}/ρ , and specific energy release rate, G_{Ic}/ρ , respectively, for various compositions of syntactic foam. The actual fracture toughness, K_{Ic} , together with the void content are presented in Table 4.1. The most distinctive features in Figure 53 are the significant increase in K_{Ic}/ρ for filler content up to 30 vol% for all types of microspheres, and the decrease in K_{Ic}/ρ beyond 30 vol% of filler content. The maximum in the trend for the fracture toughness has been reported for other solid particulate composites [73,131,135]. The increase in K_{Ic}/ρ for 0–30 vol% filler content suggests the presence of a toughening mechanism which increases the fracture energy compared to neat epoxy resin. For K_{Ic} , the hollow glass microspheres outperform the hollow phenolic microspheres with K46 microspheres resulting in the highest value for K_{Ic}/ρ , suggesting that the wall thickness and density of the microspheres affect the fracture toughness of the syntactic foam. However, the hollow phenolic microspheres outperform the hollow glass microspheres for the specific energy release rate. This is mainly caused by the lower value of the Young's modulus of the BJO-093 samples.

Effect of Porosity

(a)

(b)

Figure 52: SEM micrograph of the fracture surface of syntactic foam containing 10 vol% K15 microspheres under (a) tension, and (b) compression. The black arrows denote the direction of crack propagation.

Effect of Porosity

Figure 53: Specific fracture toughness for various compositions of syntactic foam

Figure 54: Specific critical energy release rate for various compositions of syntactic foam

4.3.2 Toughening mechanisms

Based on maximum value for K_{Ic} and G_{Ic} , as observed in Figure 53 and Figure 54, respectively, the author believes that the type of major toughening mechanism has changed at the transition point of 30 vol% of microsphere content. SEM was used to elucidate the toughening mechanisms in the various microstructures of syntactic foam.

Figure 55 shows the fracture surface of pristine epoxy resin after being subjected to 3PB. The featureless fracture surface of epoxy resin is indicative of the well-known brittle deformation of epoxy resin. Uniformly oriented white lines on the fracture surface suggest minor shear deformation of the epoxy resin prior to fracture.

It is well understood that the fracture surface of brittle particulate-filled composites can be divided in three areas, namely, pre-crack, process zone and fast fracture zone. The pre-crack zone is created by tapping a fresh razor blade into a pre-notch. The sharp crack is required to eliminate any deformation induced by the introduction of the pre-notch. Measurements performed on the size of the pre-crack elucidated that the size of the pre-crack is around 100 μm . The process zone is the area where the crack undergoes stable sub-critical crack growth. The process zone is considered as the most important area of the fracture surface in terms of contribution to the overall fracture toughness. An example of a fracture surface of a syntactic foam containing 5 vol% K46 microspheres showing the pre-crack zone (A), process zone (B), and fast-fracture zone (C), is shown in Figure 56. The gentle roughness of the fracture surface, as shown in Figure 56 is caused by the so-called step structures, which are shown

Effect of Porosity

Figure 55: Fracture surface of epoxy resin

Figure 56: Fracture surface of syntactic foam SENB specimen

Effect of Porosity

at a higher magnification as diagonal lines in Figure 57-58. In particular the tail structure behind the hollow glass microspheres can be clearly identified. The characteristic tail structure which is created by the mismatch between two planes of crack propagation is often regarded to be the evidence for the action of the crack front bowing mechanism. The mismatch between the two crack planes is clearly visible in Figure 58. Lange [76] first proposed the crack front bowing mechanism. The mechanism proclaims the resistance of rigid particles to crack propagation. Because of the impenetrability of the particles, the primary crack has to bend between particles. There will be a point when the crack front breaks away from the rigid particle. At this point, the arms of the secondary crack fronts will come together and form a characteristic step structure as both secondary crack fronts propagate at a different crack plane. These characteristic step structures are also called 'tails' or 'lances'. Many studies on the fracture toughness of particulate composites consider the crack bowing as the main toughening mechanism. The bowed secondary crack front has more elastic energy stored than the straight unbowed crack front. Therefore, more energy is needed for a crack to propagate. A clear example of the crack front bowing mechanism is shown in Figure 59. For the most right debonded microsphere, it is clearly visible that the crack has propagated over the microsphere-matrix interface and changed its direction while propagating over the interface. The change in direction causes a longer crack path and thus a higher fracture toughness.

Effect of Porosity

Figure 57: Step structures on the fracture surface

Figure 58: High magnification of a step structure

Figure 59: Debonded microspheres and step structures

Besides the presence of step structures, debonding of microspheres is observed on the fracture surface of syntactic foam, see Figure 59 and Figure 60. Debonding can be identified by the absence of the microsphere or by a gap in between the microsphere and the matrix, as indicated in Figure 60. According to [70], the debonding as shown in Figure 60 is typical for microspheres with a size larger than 10 μm . The presence of debonding of microspheres from the polymer matrix suggests the weak interfacial adhesion at the microsphere-matrix interface. Several researchers have suggested that the debonding of glass beads is one of the major toughening mechanisms or is a mechanism, which triggers matrix plastic deformation in glass bead reinforced polymers. According to Evans et al. [78] debonding of glass beads was the most prominent mode of micro-cracking in glass bead filled epoxies as it exhibited the ability to reduce the crack driving

Figure 60: SEM image of broken microsphere

force resulting in toughening behavior. The theory of debonding and matrix plastic deformation show similarity with the presence of cavitations of rubber particles and matrix shear yielding in rubber toughening of polymers [136]. Debonding involves energy dissipation and will thus impede the crack growth process.

Figure 61a and Figure 61b show the fracture surface of syntactic foam containing low and high volume fractions of microspheres, respectively. Clearly, Figure 61a shows that step structures prevail for the microstructures containing low volume fractions of microspheres. Looking at the absolute values of K_{Ic} , see Table 4.1, hollow glass microspheres exhibit higher fracture toughness compared to hollow phenolic

Effect of Porosity

(a)

(b)

Figure 61: SEM micrograph of the fractured surface of SENB specimens of syntactic foam containing hollow phenolic microspheres: (a) 10 vol%, (b) 50 vol%.

Effect of Porosity

microspheres, with K46 microspheres outperforming K15 microspheres. It is surmised that the thickness-to-radius ratio and the wall material of the microsphere affect the size of the step structure and thus K_{Ic}/ρ .

Figure 61b shows the microstructures of syntactic foam containing 50 vol% hollow phenolic microspheres. Compared to Figure 61a, step structures are absent in Figure 61b. Instead, the dominant fracture mechanism that is observed is debonding of microspheres. According to Lee and Yee [73], the increase in microsphere content will decrease the inter-particle separation between microspheres. The increase of microsphere content beyond the complete wetting ability of epoxy also introduces inter-sphere sliding. Higher volume fractions of microspheres allow more microspheres to debond from the matrix. Debonding is accompanied by premature cracks. If the direction of these cracks is parallel to the crack growth direction, the sub-critical cracks act as precursors, and facilitate crack propagation.

Now an explanation has been given for the maximum is fracture toughness vs. microspheres content curve, leaves an explanation for the increase in the fracture for syntactic foams containing 0 – 30 vol% microspheres. Comparing Figure 55, Figure 61a, and Figure 62, it is clear that similar toughening mechanisms can be observed for syntactic foam with higher volume fractions of hollow phenolic microspheres. The distinctive features observed are that the length of the step structure and the intensity of the tail structures have now increased due to the larger numerical density of microspheres

Figure 62: SEM micrograph of the fractured surface of SENB specimens of syntactic foam containing 20 vol% hollow phenolic microspheres.

causing the fracture toughness to increase with an increase in volume fraction of the microspheres.

For some syntactic foams with higher volume fractions of microspheres crushed microspheres become evident. An example of a crushed microsphere was already given in Figure 60. The presence of crushed microspheres were scarce and not concentrated in particular areas. The author believes that the crushing of the microspheres is purely attributed to the fracture behavior of the composite and not to processing conditions. Once the microspheres crush, energy is dissipated in shattering the microsphere, resulting in relief of triaxial tension and crack path deflection, attributing to the overall fracture

Effect of Porosity

toughness of the syntactic foam. From measurements done in Figure 60, it can be shown that the microsphere wall thickness is approximately 1 μm .

4.4 Impact Behavior

The impact behavior was only studied for syntactic foam containing hollow glass microspheres. A typical result of the Charpy impact tests is shown in Figure 59. Similar to the conclusion drawn for syntactic foam subjected to tensile and flexure loading shows that syntactic foam behaves like a brittle material under dynamic loading. After the maximum load, the transducer signal damps very rapidly resulting in low fracture energy, which indicates that the material fractures catastrophically following the maximum load. The oscillations are produced by the inertial forces caused by the

Figure 63: Typical result of a Charpy Impact test on syntactic foam

Effect of Porosity

Figure 64: Impact resistance of syntactic foam containing K15 and K46 microspheres for $a/W=0.25$

acceleration imparted to the specimen [137]. The impact resistance as a function of the microsphere volume fraction is plotted in Figure 64. It is clear that the impact resistance decreases due to the presence of the microspheres. The decrease in impact resistance is not affected by the type and volume fraction of microspheres. The decrease is most likely caused by the introduction of the microspheres that produce stress concentrations and constrain plastic flow in the polymer. Given the speed of impact, the polymer performs rather consistently regardless of the type and volume fraction of the microspheres.

Effect of Porosity

Figure 65: Fracture surface of syntactic foam after being subjected to a dynamic impact.

Figure 65 shows the fracture surface of syntactic foam after it has been dynamically impacted. The black arrow in Figure 65 indicates the direction of crack propagation. Similar to the SEM micrographs seen for the quasi-static three-point-bending specimens, step structures can be identified. However, the surface is more rugged for the dynamically impacted specimens, indicating the higher energy involved in fracturing the specimens. Similar to quasi-static three-point-bending tests, the intensity of the steps reduces further away from the sharp crack.

4.5 Thermal properties

4.5.1 Thermal Stability

Thermal stability is an important parameter dictating materials performance. So far no reports have been published on the effect of microspheres on the thermal stability of syntactic foam. A thermo gravimetric analysis was carried out to ascertain whether addition of microspheres affects the thermal stability of syntactic foam.

Although Figure 66 only shows the results for syntactic foam containing hollow phenolic microspheres, the results are representative for all other types of microspheres. Clearly, Figure 66 shows that the thermal stability of syntactic foam is not affected by the addition of microspheres. All microstructures have lost about 50% of their weight around 385 °C. The only difference between the different microstructures is their behavior beyond the degradation temperature. The amount of residue increases with the amount of microspheres dispersed in the epoxy resin. The thermal decomposition is completed at 550-600 °C. As the curve for pure epoxy resin is similar to the ones with microspheres

Effect of Porosity

Figure 66: Thermal stability of syntactic foam containing epoxy resin and hollow phenolic microspheres.

content, it can be concluded that the thermal stability of syntactic foam is primarily governed by the matrix of the syntactic foam.

4.5.2 Dynamic Mechanical Analysis

Figure 67 shows a similar trend as observed for the Young's modulus. The storage modulus of syntactic foams containing K15 and BJO-093 microspheres decreases with increasing microsphere content, whereas syntactic foam containing K46 microspheres shows an increase in the storage modulus with increasing microsphere content. The

Effect of Porosity

Figure 67: Storage modulus of syntactic foam with various microspheres content.

Figure 68: Glass transition temperature of syntactic foam with various microsphere content.

Effect of Porosity

difference in the behavior of the different microspheres is again attributed to the microsphere material property and wall thickness.

Figure 68 shows that the glass transition temperature, T_g , of syntactic foam slightly reduces with the inclusion of microspheres. The reduction in T_g is almost similar for all types of microspheres.

CHAPTER 5

SHORT FIBER-REINFORCED SYNTACTIC FOAM

5.1 Introduction

Short fiber toughening, whereby short fibers are dispersed in a polymeric material, is a technique that has been widely used for reinforcement efficiency and toughening of polymeric materials [138-140]. Generally, short fibers can toughen the polymer matrix via crack deflection and enhanced matrix deformation, and less so for fiber breakage and fiber pull-out due to the less than effective fiber lengths to induce breakage and optimize pull-out work. A critical advantage for fiber toughening in comparison to rubber toughening is that concomitant increase in toughness and stiffness can be accomplished only by the former.

Although syntactic foams have been studied for over three decades, short-fiber reinforced syntactic foams (SFRSF) have not been well investigated. Most of the publications on short fiber reinforced syntactic foam report the effect of the fibers on the compression and flexural behavior of short fiber reinforced syntactic foam [56,141-146]. Generally, these reports depict a synergistic behavior of SFRSF improving the compressive and flexural properties of syntactic foam.

Short Fiber Reinforced Syntactic Foam

Little is understood about the effect of the short fibers on the tensile and fracture properties of syntactic foam. This chapter reports on the studies that have been performed to evaluate the toughening potential via hybrid reinforcements using SFRSF. The effect of the carbon fiber content as well as the carbon fiber length on the tensile, fracture and thermal properties of syntactic foam will be discussed. Fracture mechanics and microscopic techniques are employed. The results will be discussed in light of known toughening.

5.2 Processing Conditions

The syntactic foam for this research was produced by mechanical dispersion of hollow microspheres in epoxy resin. Phenoset BJO-093 hollow phenolic microspheres were used for the filler. The amount of microspheres was fixed at 30 vol% as this reflected the highest fracture toughness of syntactic foam in the previous chapter. Again Epicote 1006 epoxy resin was used as the binder. Commercially available short carbon fibers (SCF) were used as the fiber reinforcement. The SCF were cut by hand from a 0°/90° carbon fiber mat. The fiber is on average 7 μm in diameter. To study the effect of the fiber length on the tensile and fracture properties, fibers with three different lengths were cut from the 0°/90° carbon fiber mat. The distribution of the fiber lengths was analyzed by measuring the fiber length from a digital image using the public domain software ImageJ [147]. The number average distributions of the fiber lengths are shown in Figure 69a-c. The mean fiber lengths are 3.11, 4.50, and 10.05 mm, respectively.

Short Fiber Reinforced Syntactic Foam

(a)

(b)

Short Fiber Reinforced Syntactic Foam

(c)

Figure 69: Fiber distributions of three different average fiber lengths; (a) 3.11 mm, (b) 4.50 mm, (c) 10.0 mm.

To study the effect of the fiber weight fraction on the tensile and fracture properties, 1, 2, and 3 wt% SCF were added to the epoxy resin. The SCF were added to the epoxy resin, followed by microspheres. This mixing order results in a reduction of the air bubbles present in the curing process as the microspheres easily position themselves in between the fibers. The microspheres were added in multiple steps to the epoxy resin to avoid agglomeration. Previously, we observed that for pristine syntactic foam the microspheres showed a tendency to float to the top surface due to their low density compared to the binder. This effect was minimal for SFRSF due to the increased viscosity of the mixture and by stirring the mixture close to the gel time, which was about

Short Fiber Reinforced Syntactic Foam

60 min, for the epoxy. Scanning electron micrographs (SEM) confirmed the homogeneity of the SFRSF. After dispersion, the SFRSF was compression molded using an aluminum mold coated with a silicone release agent. The mixture was left under the press at a pressure of 1.6 MPa for 18-22 hr to cure at room temperature.

Due to hand mixing, the short fibers are randomly dispersed. The distribution of the fiber angles was obtained using the method presented by Norman and Robertson [68]. The fiber angle distribution was measured from optical micrographs of polished sections using ImageJ [147] available on the public domain on digitized images. Planar fiber angle distributions for the nonaligned specimens are shown in Figure 70. The planar fiber angle distributions were converted to three dimensions by assuming the distributions to be symmetric about the field axis. Figure 71 shows the general microstructures of SFRSF.

Figure 70: Fiber angle distribution of short-fiber-reinforced syntactic foam

Short Fiber Reinforced Syntactic Foam

Figure 71: General microstructure of short carbon fiber-reinforced syntactic foam.

5.3. Effect of the fiber content and fiber length on various properties

5.3.1 Tensile Properties

SFRSF behaves like a linear elastic material up to failure when loaded in tension. This conclusion is drawn based on observations performed on the fractured samples. All samples show a catastrophic failure across a plane perpendicular to the loading direction. The tensile properties of SFRSF reinforced with various amounts of short fibers are shown in Figure 72a and b. It is clear that the SCF improve the tensile strength, σ_t , as

Short Fiber Reinforced Syntactic Foam

well as the Young's modulus, E_t of SFRSF. As shown in Figure 72a, the ultimate tensile strength, σ_{uts} , increases by 40% with the addition of only 3 wt% SCF. The increase is similar for the various fiber lengths examined. The trend of σ_{uts} with the fiber content is consistent with the data presented by other investigators for short fiber reinforced polymers [68,148,149]. For the Young's modulus, E_t , see Figure 72b, a linear additive trend with the increase in SCF weight fraction is observed. E_t increases from 1.58 GPa for neat syntactic foam to 3.4 GPa for syntactic foam containing 3 wt% SCF, an increase of 115%. Similar to σ_{uts} , the fiber length variation does not affect the E_t of SFRSF.

It is understood that the tensile strength can be influenced by fiber orientation. Compared to unidirectional fiber reinforcement, random orientation of the short fibers is known to result in lower reinforcement effectiveness in fiber reinforced polymeric materials [68,148-151,]. The contrast for reduction in E_t due to random fiber orientation is given in Figure 72b. The linear additive trends as shown are considerably and consistently lower than the rule-of- mixtures. The curve for the rule-of-mixtures is estimated by assuming that carbon fibers alone are unidirectional aligned and exhibit a Young's modulus of 228 GPa [152]. From the elementary composite mechanics theory, see Figure 73, the following equation for the effective fiber length, $\bar{l}$, is derived:

$$\bar{l} = \frac{N \int_0^{\pi/2} \int_0^{\pi/2} l \cos \theta \cos \varphi d\theta d\varphi}{N \left(\frac{\pi}{2} \right)^2} = 0.41l \quad (5.1)$$

Short Fiber Reinforced Syntactic Foam

(a)

(b)

Figure 72: Tensile properties of short carbon fiber reinforced syntactic foam with different fiber weight fractions and fiber lengths: (a) Tensile strength, (b) Young's modulus

Short Fiber Reinforced Syntactic Foam

Figure 73: Angles of fiber orientation. From [148]

where, N is the number of fibers, l the fiber length, θ and ϕ are the projected angles on the loading axis, x , and x - y plane, respectively, in 3D orientation. The result of the integration of Equation 5.1 shows that only 41% of fiber lengths are effective for reinforcement in three dimensional (3D) randomly orientated fibers.

Figure 72b shows that the experimental data obtained from the tensile tests demonstrate slightly better fiber length efficiency in comparison to the average value of 41% given by Equation 5.1. Based on a calculation of the slopes of the experimental data, it is determined that SFRSF exhibits an average efficiency of about 48%. A random fiber orientation of SCF in the current SFRSF system is unavoidable since the components are mixed by hand in a beaker and poured directly into an open mould.

Short Fiber Reinforced Syntactic Foam

Figure 72a and b indicate that the difference in fiber length does not cause a large variation in the tensile properties. With a simple estimation, it is demonstrated that the critical fiber transfer length, l_c , is exceeded by the shortest fiber length introduced [153]:

$$l_{crit} = \frac{d\sigma_{fb}}{2\tau_y} \quad (5.2),$$

where, σ_{fb} is the fiber strength, d is the fiber diameter, and τ_y is assumed to be the matrix shear strength, which is assumed to be close to $\tau_y = \sigma_{my}/2$; σ_{my} is the matrix yield

Figure 74: SEM image of short carbon fibers

Short Fiber Reinforced Syntactic Foam

strength. Measurements using SEM, see Figure 74, show that the SCF used for the current research have an average diameter of 7 μm . Based on this diameter, the critical fiber length, l_{crit} , is estimated to be 0.2 mm. Note that Equation 5.2 assumes a strong fiber-matrix interface and unidirectional fiber alignment. Fiber end bonding is also ignored. These two assumptions are both violated in the current study. However, it could be understood that the current fiber lengths of 3, 4.5, and 10 mm are likely to be compatible if not exceeding l_{crit} .

Similar conclusions were drawn by Chen and Cheng [150]. It was concluded that the effective elastic modulus became more or less constant for a composite reinforced

Figure 75: The fiber orientation factor λ dependence of the elastic moduli as functions of aspect ratio at $V_{fb} = 0.3$ [150].

Short Fiber Reinforced Syntactic Foam

Figure 76: SEM image of the fracture surface of short carbon fiber-reinforced syntactic foam subjected to tensile loading.

with fibers having a length-to-diameter ratio, l/d , of about 40 - 80, see Figure 75. For the 3, 4.5 and 10 mm short carbon fibers, the values for l/d is 428.5, 642.9, and 1428.6, respectively. The l/d values for the SCF are far bigger than those reported by [150]. The l/d values for all the fiber length are located on the horizontal limit which explains that a change in the fiber length ranging from 3 to 10 mm does not have any effect on the Young's modulus.

In order to establish the individual contribution of the SCF and hollow microspheres to the tensile properties of SFRSF, a series of tensile tests were performed on epoxy resin reinforced with 10 mm SCF. The tests were only performed on one length

Short Fiber Reinforced Syntactic Foam

of SCF since the above results have shown that the length of the SCF does not affect the tensile behavior of SFRSF. The results of the tensile behavior of SFRE are shown in Figure 72a and b. Figure 72a shows that the tensile properties of SFRE are superior compared to those of SFRSF. The slope of the curve for SFRE is much steeper than that for SFRSF, indicating the higher efficiency of the SCF in SFRE. Compared to pristine epoxy resin, an addition of 3 wt% of SCF to epoxy resin increases the tensile strength by 68%. The increase in strength is attributed to the bridging effect of the SCF. Addition of 3wt% of SCF to syntactic foam increases the tensile strength only by 36%, a reduction of 32% compared to SFRE. Similar results are observed for the Young's modulus, see Figure 72b. SFRE shows a higher Young's modulus compared to SFRSF. The reduction in strength and modulus of SFRSF is attributed to the presence of the microspheres. It can be concluded that microspheres act as some kind of pores under tensile loading. Despite the weakening effect of the microspheres, it should be noted that the tensile properties of SFRSF still increase with increasing SCF content, indicating the potential of SFRSF.

Fractographic examinations of tested SFRSF tensile specimens, see Figure 76, show the various toughening mechanisms present in SFRSF. Fractured and debonded fibers, matrix deformation, debonded microspheres and crushed microspheres are observed. Figure 76 also confirms the random orientations of the SCF because both fibers orientated perpendicular to the fracture surface and fibers orientated parallel to the fracture surface can be observed. Clearly, the matrix around the SCF shows increased deformation compared to areas without fibers. The fibers are significantly stronger than

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the microspheres and are likely to bear a higher effective load. Once the fiber breaks and debonds, the energy is transferred to the matrix and microspheres causing further damage. The toughening effect arising from fiber reinforcement is evident in Figure 72.

5.3.2 Thermal properties

Figure 77 shows that the thermal stability of SFRSF is independent of the fiber length and fiber weight fractions. For all the samples tested, a substantial weight loss is observed around 350 °C. The thermal decomposition is completed at 550-600 °C. As the curve for 0 wt% SCF is similar to the ones with SCF content, it can be concluded that the thermal stability of SFRSF is primarily governed by the matrix of the SFRSF.

Figure 78a and b show the results from dynamic mechanical analysis (DMA). Figure 78a shows the effect of the fiber content and fiber length on the storage modulus, E' . Similar to the results, previously shown for Young's modulus, see Figure 72b, the storage modulus increases with the short fiber content. A clear trend with the fiber length is, however, not observed. Despite a slight increase in the glass transition temperature, T_g ,

Short Fiber Reinforced Syntactic Foam

Figure 77: Weight loss vs. temperature for short carbon fiber reinforced syntactic foam with different fiber weight fractions and fiber lengths.

compared to neat syntactic foam, it is clear from Figure 78b that the variations in fiber content and fiber length do not affect the T_g of SFRSF. The peak in the $\tan\delta$ vs. temperature curve, which is considered to be indicative for T_g , is located around 69 °C for all samples.

5.3.3 Fracture Properties

Figure 79a and b show the interesting results of the fracture toughness assessment on SFRSF. The most distinctive feature in Figure 79a, is the increase in the plane strain fracture toughness, K_{Ic} , with increasing fiber content. The results strongly suggest the

Short Fiber Reinforced Syntactic Foam

(a)

(b)

Figure 78: (a) Storage modulus and (b) $\tan \delta$ vs. temperature for short carbon fiber reinforced syntactic foam with different fiber weight fractions and fiber lengths.

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synergistic benefit of fiber reinforcement in syntactic foam. It is evident concomitant increases in both tensile strength and fracture toughness can be accomplished in a hybrid system. K_{Ic} increases from $1.15 \text{ MPa}\cdot\text{m}^{0.5}$ of neat syntactic foam to $2.25 \text{ MPa}\cdot\text{m}^{0.5}$ of a composition containing 3 wt% fibers, an impressive increase of about 95%. At present, it is not clear why K_{Ic} shows different values for different fiber lengths at 2 wt% reinforcement. Fracture toughness is governed essentially by the local deformation events such as one embedded in a fracture process zone, and is less dependent on the global properties as compared to stiffening and strengthening mechanisms. Interactions between the reinforcing components including SCF and microsphere, and the epoxy matrix are complex. Thus, a clear explanation of the varying fracture toughness awaits more microscopic evidence.

For 1 wt% and 3wt% fibers, the effect of the fiber lengths on the fracture properties appears to be less pronounced. This observation is in line with the work reported by Chiang [154] who highlighted that the fracture toughness reaches a limit if the fiber reaches the critical fiber length.

The critical energy release rate, G_{Ic} , which is calculated from the K_{Ic} and the respective Young's modulus data, is shown in Figure 79b. Despite the deviation in results for 2 wt% SCF reinforcement, a general increasing trend in G_{Ic} is observed when the fiber content is increased from 0 to 3 wt%. Increase in both K_{Ic} and G_{Ic} indicate the excellent toughening potential of SCF in syntactic foams.

Short Fiber Reinforced Syntactic Foam

(a)

(b)

Figure 79: Effect of fiber content and fiber length on the fracture properties of short carbon fiber reinforced syntactic foam; (a) critical stress intensity factor, K_{Ic} , (b) critical energy release rate, G_{Ic} .

Short Fiber Reinforced Syntactic Foam

An SEM fractograph of a SENB specimen is shown in Figure 80. The black arrow denotes the direction of crack propagation. Various toughening mechanisms, including fiber pull-out, fiber breakage, step structures, debonding of microspheres and fractured microspheres are identified. Optical microscopy (OM) was performed to evaluate the possible presence of micro-shear banding as reported by Lee and Yee [70,71]. Micro-shear banding has been reported as an important toughening mechanism in glass sphere reinforced polymers. An image of the sharp crack and crack initiation region obtained with a transmission optical microscope (TOM) is shown in Figure 81. The image clearly shows the presence of fiber bridging and debonding of microspheres at the crack interface. Despite observing multiple specimens containing different amounts of reinforcing fibers under the optical microscope, no micro shear banding can be seen under polarized light. The absence of the microshear banding could be related to the epoxy resin used as Lee and Yee mentioned that microshear banding could be absent in brittle matrices.

The presence of multiple toughening mechanisms on the fracture surface of SENB specimens requires an in-depth analysis to determine the contribution of each toughening mechanism to the overall toughness of the composite. The presence of fiber breakage, interface debonding and pull-out suggests the presence of fiber bridging during the fracture process. Fiber bridging is known to be a major toughening mechanism in fiber reinforced polymer composites. As the crack front approaches, it is halted by the fiber and shows a tendency to circumvent the crack face in the transverse direction,

Short Fiber Reinforced Syntactic Foam

Figure 80: SEM image of the fracture surface of an SENB specimen of short fiber reinforced syntactic foam.

Figure 81: Transmission optical micrograph showing the subsurface damage near the sharp and initiation crack area in short carbon fiber reinforced syntactic foam. The black arrow indicates the direction of crack propagation.

Short Fiber Reinforced Syntactic Foam

causing interfacial debonding between the fiber and the matrix. The contribution of the interfacial debonding toughness, R_d , to the overall SFRSF toughness can be estimated by using the following equation [153]:

$$R_d = \frac{V_{fib} \sigma_{fib}^2 l_d}{2E_{fib}} \quad (5.3),$$

where V_{fib} is the volume fraction of SCF, l_d the debonding length, and E_{fib} the Young's modulus of the SCF. Values for R_d obtained for SFRSF containing various amounts of SCF are given in Table 5.1. It is obvious that the interfacial debonding is poor which is confirmed in Figure 80, where the fiber surface appears to be very clean of matrix materials, indicating a poor interface between the matrix and the fibers.

After the interfacial debonding, fibers can either debond from the matrix or fracture in the crack plane, depending on the fiber aspect ratio. According to Hull and Clyne [155], debonding of all the fibers occurs if the fiber aspect ratio, s ($= l/d$), is below a critical value. The critical value, s_{crit} , can be calculated using the following equation [155]:

$$\sigma_{crit} = \frac{\sigma_{fib}}{2\tau_m} \quad (5.4),$$

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where τ_i is assumed to be the matrix shear strength. For the SCF dispersed in the SFRSF, s_{crit} is estimated to be 28.2. Based on a fiber diameter of 7 μ m, the fiber aspect ratios for the three different fiber lengths of 3, 4.5 and 10 mm, are estimated to be 429, 714, and 1428, respectively. It is obvious that s_{crit} is only a fraction of s for all three fiber lengths indicating that the SCF in SFRSF will fracture in the crack plane instead of fully debonding from the matrix. Fracture of the fibers will prevail since there will always be embedded lengths on either side of the crack plane which are long enough for the stress in the fiber to build up sufficiently to break the fiber. According to [155], the actual fiber breaking makes little or no direct contribution to the overall toughness. Typical fracture energies for carbon fibers are only a few tens of J.m⁻².

Though the actual breaking of the fiber is expected to have a minor effect on the overall fracture toughness of the fiber-reinforced composite, it is believed that the redistribution of the strain energy that occurs when a fiber breaks might have more impact on the overall toughness. According to Kim and Mai [153], the toughness due to the redistribution of the strain energy stored in the fiber prior to fracture, R_r , can be calculated with the following equation:

$$R_r = \frac{V_{fib} \sigma_{fib}^2 l_{crit}}{3E_{fib}} \quad (5.5),$$

Table 5.1 shows the conjectural estimates for R_r and several other toughness contributions. The relative contribution from each mechanism is shown by bracketed

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values. Clearly R_r is relatively low which is mainly caused by the low volume fraction of SCF in SFRSF.

Despite the fact that fibers show the preference to fracture in the crack plane, debonding and pull-out of fibers can be observed on the fracture surface of SENB specimens, see Figure 80. However, the contribution of debonding to the overall toughness is minimal as the debond length, as estimated from SEM images, is only in the order of tens of micrometers. It should be noted that the amount of debonding is related to the fiber orientation. Fibers orientated perpendicular to the crack plane show the smallest debonding length. The contribution of the fiber pull-out toughness, R_{po} , to the toughness of SFRSF can be estimated as follows [153]:

$$R_{po} = \frac{V_{fib} \tau_{fr} l_{crit}^2}{6d} \frac{l_{crit}}{l} \quad (5.6),$$

where τ_{fr} is the frictional shear stress. Please note that Equation 5.6 is for unidirectional fibers having a length greater than the critical fiber length. Table 5.1 shows the minor contribution of fiber debonding to the overall toughness of SFRSF.

It is clear from Figure 80 that localized matrix yielding occurs near fiber ends. In addition, step structures can be observed behind many of the fibers. The quantity and intensity of the step structures observed on the fracture surface of SFRSF seems to be

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more significant compared to pristine syntactic foam, as observed in the previous chapter. These step structures are the result of the crack front bowing mechanism as proposed by Lange [76]. The crack front bowing mechanism has been discussed in depth in the previous chapter. Many studies on the fracture toughness of particulate composites consider the crack bowing mechanism as the main toughening mechanism. The main aspect responsible for the absorption of the energy is the formation of new surfaces. The contribution of the toughness due to the formation of new surfaces, R_s , to the overall toughness of fiber reinforced composites is discussed by Marston et al. [156] and Atkins [157]. R_s is regarded as the sum of the specific energies absorbed in creating new surfaces in fiber, matrix and at the interface. For SFRSF, additional surfaces are created in microspheres. To account for the additional microsphere surfaces, the equation given by [157] has been modified by replacing the matrix toughness with the toughness of pristine syntactic foam containing 30 vol% phenolic microspheres, R_{sf} . R_s can be calculated with the following equation:

$$R_s = V_{fib} R_{fib} + (1 - V_{fib}) R_{sf} + \frac{V_{fib}}{l_{crit}} R_{ic} \quad (5.7).$$

By assuming that the fiber toughness, R_{fib} , is negligible and the interfacial fracture toughness, R_{ic} , is equal to the toughness of pristine syntactic foam, R_{sf} , Equation 5.7 can be re-written to the following:

Table 5.1: Conjectural estimates of toughening contributions from interfacial debonding, R_d , strain redistribution energy, R_r , fiber pull-out, R_{po} , and formation of new surfaces R_s , to the total toughness of short-fiber reinforced syntactic foam. The relative % from each contribution is indicated by the bracketed value.

SCF Weight Fraction (wt%)	SCF Volume Fraction (vol%)	R_d (kJ/m ²)	R_r (kJ/m ²)	R_{po} (kJ/m ²)	R_s (kJ/m ²)	R_t (kJ/m ²)
0	0	NA	NA	NA	0.736 (100%)	0.736
1	0.48	0.0006 (~0.07%)	0.0082 (~0.96%)	0.0122 (~1.43%)	0.8334 (~97.54%)	0.8544
2	0.97	0.0012 (~0.12%)	0.0164 (~1.68%)	0.0245 (~2.52%)	0.9319 (~95.68%)	0.9740
3	1.46	0.0019 (~0.17%)	0.0247 (~2.26%)	0.0370 (~3.38%)	1.0313 (~94.19%)	1.0949

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$$R_s = \left[V_{fib} \left(\frac{l_{crit}}{d} - 1 \right) + 1 \right] R_{sf} \quad (5.8).$$

The estimated values for R_s can be found in Table 5.1. It is obvious that the specific energy required for the formation of new surfaces is significantly higher compared to the other toughening mechanisms discussed and can, thus, be considered as the main toughening mechanism in SFRSF.

The total toughness of SFRSF, R_t , is now estimated by combining the contributions of each individual mechanisms. $R_t = R_d + R_r + R_{po} + R_s$. Figure 79b reflects the result of R_t for various weight fractions of SCF. It is clear that the conjectural estimate of R_t , as discussed, represents the trend and values for the experimentally measured critical energy release rate vs. weight fraction of SCF quite closely.

Again to determine the individual contribution of the SCF and hollow microspheres to the fracture properties, a series of fracture tests were performed on epoxy resin reinforced with 10 mm long SCF. The K_{Ic} and G_{Ic} values of SFRE are shown in Figure 79a and b, respectively. For both SFRE and SFRSF, the fracture toughness, K_{Ic} , increases 136% and 100%, respectively, with the addition of 3wt% of SCF. However, SFRSF shows a constant higher fracture toughness compared to SFRE for all contents of SCF. This result is interesting as it shows the synergism between hollow microspheres and SCF for the fractural behavior of SFRSF. Based on the results presented in Figure 79, it has been calculated that the addition of hollow spheres increases the K_{Ic} of SFRSF by

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Figure 82: SEM image of the fracture surface of an SENB specimen of short fiber reinforced epoxy

39% to 18% for 0wt% and 3wt% reinforcement of SCF, respectively. Besides the increase in K_{Ic} , Figure 79 also shows that SFRSF also exhibits a constant higher G_{Ic} compared to SFRE.

Figure 82 shows an SEM fractograph of a SFRE SENB specimen. Comparing Figure 82 to Figure 80, it is obvious that the fracture surface of SFRE is more smooth compared to that of SFRSF. An increased number of step structures, especially behind microspheres, are observed on the fracture surface of SFRSF. It is also observed that the step structures behind the fibers tend to be longer for SFRSF as the step structures move towards the nearest/biggest microsphere, whereas for SFRE, the step structures tend to end at a random location on the fracture surface. In addition, for SFRSF, the

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microspheres debond from the matrix which is also energy absorbing. The presence of extra step structures in combination with the debonding of the microspheres is likely to be the reason for the improved fracture properties of SFRSF compared to SFRE.

CHAPTER 6

NANOCLAY-REINFORCED SYNTACTIC FOAM

6.1 Introduction

Over the past decade nanotechnology has proven to be an excellent method of increasing the mechanical and fracture properties of materials [103,104]. Especially, inclusion of nanoclay particles in polymeric materials has been proven to elucidate remarkable property enhancements [92-112]. The enhancements in the tensile, fracture and thermal properties are attributed to the high aspect ratio of the silicate nanolayers. Largest improvement in properties is observed for those nanocomposites where the polymer is able to penetrate and expand the gallery in between two clay layers. This is referred to as exfoliation. Often the polymer only slightly expands the gallery which is called intercalation. Though both intercalated and exfoliated nanoclay layers are able to improve the properties of the nanocomposites, the highest improvements have been observed for exfoliated nanoclay layers.

Despite being proven to be an effective reinforcement for polymers, nanoclay-reinforced syntactic foam (NCRSF) has been hardly unexplored [158-160]. Gupta et al. have reported some work on the effect of nanoclay on the flexural properties of syntactic foam but knowledge of the fracture, microdeformation and mechanics of nanoclay-reinforced syntactic foam is rather vague. As nanoclay layers are able to increase the

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fracture toughness of polymers, the author believes that it is interesting to study the effect of nanoclay layers on the fracture properties of syntactic foam. As the nanoclay particles have the ability to settle in between the microspheres, it would be interesting to evaluate a possible synergistic behavior in a hybrid syntactic foams comprising of a matrix, hollow microspheres, and nanoclay particles.

In this Chapter, the tensile, thermal and fracture behavior of nanoclay-reinforced syntactic foam (NCRSF) are being reported. By employing scanning and transmission electron microscopy and optical microscopy, the toughening mechanisms present in NCRSF are being discussed. The results obtained for the NCRSF nanocomposites will be compared against the results on short fiber-reinforced syntactic foam as reported in the previous Chapter. The comparison will give a better insight in the effectiveness of nano- and micro-toughening of syntactic foam.

6.2 Processing of nanoclay-reinforced syntactic foam

For all the specimens Epicote 1006 epoxy resin was used as the binder. Epicote 1006 is a combination of liquid bisphenol-A, epichlorohydrin epoxide resin, amine and polymeric additives. Phenoset BJO-093 hollow phenolic microspheres were used for the filler. The nanoclay used for this work was Nanomer I.30TC supplied by Nanocor, Inc. The physical properties of Nanomer I30TC are given in Table 6.1 . Nanomer I.30TC is a

*Nanoclay-Reinforced Syntactic Foam***Table 6.1: Physical properties of Nanomer I.30TC**

Appearance	White/Yellowish powder
Mean dry particle size	16-22
+325 Mesh residue (%)	0.1
Specific gravity (-)	2.1
Moisture (%)	3.0
Bulk Density (g/cm ³)	0.30-0.36
Purity (% min)	98.5

surface modified montmorillonite mineral. The clay was organically modified clays with octadecylammonium ion and methyl tallow bis-2- hydroethyl quaternary ammonium ion as the swelling agent. Unlike conventional mineral fillers, Nanomer I.30TC enhances performance at low loading levels, generally 1-5 wt%. This unique feature provides improved performance with minimal added weight. Low loadings minimize toughness loss and surface imperfections often encountered with conventional fillers. According to Meng and Hu [161], the interlayer spacing of the organically modified clay calculated from the wide angle X-ray diffraction (WAXD) d001-reflection was 2.4 nm. The amount of nanoclay added to the epoxy resin ranged from 0 – 2.0 wt%.

Nanoclay-Reinforced Syntactic Foam

Figure 83: Processing conditions of nanoclay-reinforced syntactic foam

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It is well understood that the method of processing epoxy/clay nanocomposites affects the quality of the epoxy/clay nanocomposites. For the dispersion of the nanoclay into the epoxy system, a mixing strategy reported by Wang et al. [162] was adopted, see Figure 83. According to [162], the mixing process or ‘slurry-compounding’ process resulted in improved exfoliation morphology for epoxy/clay nanocomposites. After the nanoclay was dispersed in the epoxy resin, a similar mixing strategy as was described in Chapter 3 for pristine syntactic foam was adopted. A stoichiometric amount of hardener and 30 vol% of BJO-093 phenolic microspheres were added to the epoxy/nanoclay mixture. The amount of microspheres was fixed at 30 vol% as this amount of microspheres elucidated the highest fracture toughness as presented in Chapter 4. The mixture was then poured into a pre-coated aluminum mold to cure under a pressure of 16-18 bars at room temperature for about 20 hours. Figure 84 shows the general structure of a nano-clay reinforced syntactic foam (NCRSF).

Figure 84: Reflective optical micrograph showing the general structure of nanoclay-reinforced syntactic foam at high magnification.

6.3. Effect of the Nanoclay Content on the tensile, thermal and fracture properties

6.3.1 Morphology

The clay morphology within epoxy is shown in Figure 85-84. Figure 85 clearly shows that clay agglomeration is present in NCRSF. The light, white area is the epoxy matrix, and the black area is made up of nanoclay layers. It has been reported that the amount of aggregation is dependent on the clay content [115]. The number of clay clusters will increase with the amount of nanoclay. Figure 86 shows a part of the aggregate, shown in Figure 85, at higher magnification. It is clear that the nanoclay layers are positioned in their preferred face-to-face alignment. By using the public domain software ImageTool [163], the thickness of the clay platelets and average distance between the platelets is estimated to be 1.0 and 3.9 nm, respectively. It is clear from Figures 80 and 81 that a nanocomposites comprising of epoxy resin and intercalated nanoclay has been synthesized. A similar kind of intercalation of the nanoclay layers is observed for specimens containing 0.75, 1.0, 1.5 and 2.0 wt% of nanoclay content. Besides intercalation, minor exfoliation, intensified disorientation and even delamination of the clay platelets is observed, see Figure 87 and Figure 88.

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Figure 85: TEM micrograph of syntactic foam reinforced with 0.5wt% nano-clay at low magnification.

Figure 86: TEM micrograph of syntactic foam reinforced with 0.5wt% nano-clay at high magnification.

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Figure 87: TEM micrograph of syntactic foam reinforced with 1.0wt% nano-clay

Figure 88: TEM micrograph of syntactic foam reinforced with 2.0wt% nano-clay

6.3.2 Tensile properties

From the fractured tensile specimens, it is observed that the addition of silicate clay particles to syntactic foam does not change the fracture behavior of syntactic foam. Similar to neat syntactic foam, a brittle fracture is observed for NCRSF. However, more than neat syntactic foam, it is observed that fracture occurs due to an oversized void. This is not uncommon as an oversized void acts as a stress concentration [39]. The author believes that the voids remain in the system, despite the degassing process and application of a pressure of 16 MPa for 18-22 hours, due to highly intercalated and exfoliated clay platelets which may form a barrier for voids to float to the surface. The presence of voids is probably one of the causes for the reduction in the tensile strength, σ_t , with increasing nanoclay content, see Figure 89a. A similar trend has been reported elsewhere [107,109,162]. Besides voids, agglomeration of the nanoclay could be another reason for the reduction in σ_t with increasing nanoclay content. The presence of relatively large micro-aggregates in the nanocomposite plates may act as stress concentrations. These clusters of nanoclay layers easily split up under an applied load, significantly lowering the tensile strength [125]. The drop in the tensile strength suggests that an improvement in the synthesis of NCRSF is required.

Figure 89b shows the results for the Young's modulus, E_t , for NCRSF reinforced with different amounts of nanoclay. E_t increases from 1.59 GPa to 1.9 GPa with the addition of 2 wt% nano clay. Kornemann et al. [125] believe that for nanoclay-reinforced polymers, the increase in E_t with increasing nanoclay content could correspond to an increase in the effective volume fraction of the reinforcement in the nanocomposite. As

Nanoclay-Reinforced Syntactic Foam

(a)

(b)

Figure 89: Tensile properties of nanoclay-reinforced syntactic foam (NCRSF) and short-fiber reinforced syntactic foam (SFRSF) with varying filler content; (a) tensile strength, (b) Young's modulus.

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the interlamellar spacing is increased, the effective particle volume fraction is also increased. Yasmin et al. [116] suggest that an increasing Young's modulus can be attributed to a better dispersion and intercalation/exfoliation of the nanoclay particles that restricts the mobility of the polymer chains under loading as well as to the good interfacial adhesion between the particles and the epoxy matrix.

Figure 90a-c show the SEM fractographs of NCRSF specimens after being subjected to tensile loading. It is clear that the fracture surface of specimens containing 1.5 wt% nanoclay, see Figure 90b, is rougher compared to the fracture surface of specimens containing 0.75 wt% nanoclay, see Figure 90a. According to [116], the rough fracture

(a)

Nanoclay-Reinforced Syntactic Foam

(b)

(c)

Figure 90: Fracture surface of nanoclay-reinforced syntactic foam subjected to tensile loading; (a) syntactic foam reinforced with 0.75 wt% nanoclay content, (b) syntactic foam reinforced with 1.5 wt% nanoclay content (low magnification), and (c) syntactic foam reinforced with 1.5 wt% nanoclay content (high magnification).

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surface is caused by the intercalated clay platelets. The intercalated platelets cause the crack to follow a tortuous fracture path. Figure 90b also shows the presence of some agglomerates of nanoclay which is in line with the previous reported findings on the reduction in tensile strength with increasing nanoclay content. A close-up of an agglomerate is shown in Figure 90c. It is clear that cracks initiate from the nanoclay agglomerate, leading to a reduction in the tensile strength.

Over the years various models have been developed to predict the Young's modulus of particle-modified polymers. One commonly used model is the Halpin-Tsai relationship [164,165]. The Halpin-Tsai model gives the modulus of the composite as a function of the matrix modulus and of the particles, but also as a function of the aspect ratio by the inclusion of a shape factor. According to Halpin-Tsai, the Young's modulus of the nanoclay-reinforced syntactic foam, E_{NCRSF} , can be estimated by using the following equation:

$$E_{NCRSF} = \left(\frac{1 + \zeta \eta V_{fib}}{1 - \eta V_{fib}} \right) E_m \quad (6.1),$$

with

$$\eta = \left(\frac{\frac{E_{fib}}{E_m} - 1}{\frac{E_{fib}}{E_m} + \zeta} \right) \quad (6.2),$$

Nanoclay-Reinforced Syntactic Foam

where ζ is a shape factor, E_{fib} is the Young's modulus of the nanoclay particles, E_m is the matrix modulus. The values taken for E_{fib} , and ζ are similar to those presented by Kinloch and Taylor [166]. It is clear from Figure 89b that the estimation of the Young's modulus of NCRSF by using the Halpin-Tsai model represents the trend and values for the experimentally measured Young's modulus vs. weight fraction of nanoclay quite closely.

A comparison has been made against tensile data for nanoclay-reinforced epoxy available in the literature. Wang et al. [162] report about the strengthening/toughening behavior of two different kinds of nanoclay, namely Cloisite 93A and S-clay, in epoxy resin. Comparing the results of nano-reinforced syntactic foam against the results of S-clay reinforced epoxy resin, see Figure 89a and 89b, it is obvious that NCRE features a superior tensile behavior compared to NCRSF. Exfoliation of the S-nanoclay is probably one of the causes of the superior behavior of NCRE. The use of a different, probably stronger, epoxy resin system could be another contributing factor.

From Figure 89a and b, it is clear that a hybrid reinforcement comprising of short carbon fibers and hollow microspheres is more effective in increasing the tensile strength and Young's modulus of syntactic foam than a hybrid reinforcement of nanoclay and hollow microspheres. Inclusion of 2 wt% of short carbon fibers (SCF) with a diameter of 7 μm increases the tensile strength and Young's modulus by 21.5% and 84%, respectively, whereas 2wt% of nano-reinforcement reduces the tensile strength by 14% and increases the Young's modulus by 17%. The difference in strengthening and stiffening effect between SFRSF and NCRSF is mainly attributed to the strength,

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Young's modulus and length of the short carbon fibers which are all far superior to those for the nanoclay particles. It should be noted that the current processing conditions of NCRSF do not lead to fully exfoliated nanoclay layers. Improved tensile properties are expected for optimized processing conditions.

6.3.3 Thermal properties

Figure 91a and b show that the thermal stability of SFRSF is independent of the fiber length and fiber weight fractions. For all the samples tested, a substantial weight loss is observed around 350 °C and the thermal decomposition is completed at

(a)

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(b)

Figure 91: (a) Weight loss vs. Temperature, (b) Weight loss derivative vs. Temperature for nanoclay reinforced syntactic foam with different nanoclay weight fractions.

550-600°C. As all the curves are similar, it can be concluded that the thermal stability of NCRSF is primarily governed by the matrix of the NCRSF.

6.3.4 Fracture properties

Figure 92a and b show the fracture toughness, K_{Ic} , and critical energy release rate, G_{Ic} , of NCRSF, respectively. Initially, a decrease in K_{Ic} is observed for specimens containing 0-0.75 wt% of nanoclay. At the moment, it is not fully clear why NCRSF shows a reduction in K_{Ic} for samples containing 0 - 0.75 wt% nanoclay. A similar drop in K_{Ic} has not been reported before. For NCRSF containing 1 – 2 wt% nanoclay particles,

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(a)

(b)

Figure 92: Fracture toughness of (■) nano-clay reinforced syntactic foam and (●) short fiber reinforced syntactic foam obtained with SEN-3PB as a function of reinforcement concentration; (a) K_{1c} ; (b) G_{1c} .

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an increase in K_{Ic} is observed compared to pristine syntactic foam. K_{Ic} of NCRSF increases from $1.15 \text{ MPa}\cdot\text{m}^{0.5}$ for 0 wt% nanoclay to $1.63 \text{ MPa}\cdot\text{m}^{0.5}$ for 1 wt% nanoclay, an increase of about 42%. The K_{Ic} value slightly drops for specimens containing more than 1wt% nanoclay. The drop is attributed to the agglomeration of the nanoclay layers.

The critical energy release rate, G_{Ic} , for syntactic foam containing various amounts of nanoclay is shown in Figure 92b. G_{Ic} is calculated from the K_{Ic} and the respective Young's modulus data. The trend in G_{Ic} vs. wt% nanoclay is similar to the trend observed for K_{Ic} as shown in Figure 92a. Introduction of 0.75 wt% causes G_{Ic} to decrease from 0.66 kJ/m^2 to 0.41 kJ/m^2 , a reduction of 41%. Compared to pristine syntactic foam, G_{Ic} shows a significant increase of 104% for specimens containing 1wt% nanoclay. The sharp increase at 1 wt% nanoclay suggests that 1wt% of nanoclay acts like a threshold; an amount of nanoclay required to induce toughening in NCRSF. The increase in both K_{Ic} and G_{Ic} for syntactic foam containing 1 wt% nanoclay indicates the excellent toughening potential of nanoclay in syntactic foams.

Comparing micro-toughening to nano-toughening, it is clear from Figure 92a and b that, in general, for similar weight fractions, micro-toughening is more effective than nano-toughening. An exception is observed for samples containing 1 wt% of nano-reinforcement. NCRSF containing 1 wt% of nanoclay elucidates a similar K_{Ic} value and an even higher G_{Ic} compared to syntactic foam reinforced with 1 wt% SCF. However, it should be noted that the processing conditions of NCRSF are not optimal. Improved

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results are expected for optimized processing conditions leading to exfoliated nanoclay layers.

A comparison has been made against fracture data for nanoclay-toughened epoxy available in the literature. Wang et al. [162] report about the toughening behavior of two different kinds of nanoclay, namely Cloisite 93A and S-clay, in epoxy resin. Comparing the results of nano-toughened syntactic foam against the results of S-clay toughened epoxy resin, see Figure 92a and 93b, it is obvious that NCRSF features a superior fracture behavior compared to nanoclay-toughened epoxy. The result suggests that an exfoliated nanoclay system might not result in the optimal fracture behavior. Agglomeration of nanoclay layers is preferred as the agglomerates are able to divert the path of crack growth and induce the formation of micro-cracking, increasing the fracture toughness. The improved fracture behavior of NCRSF over nanoclay-toughened epoxy suggests a synergistic behavior between the hollow microspheres and the nanoclay layers. Besides superior absolute K_{Ic} and G_{Ic} values, Table 6.2 shows that nanoclay-toughened syntactic foam also shows the largest relative increase in (specific) K_{Ic} and G_{Ic} compared to nanoclay-toughened pristine epoxy resin.

In order to elucidate the toughening mechanisms responsible for the fracture behavior, the fracture surfaces of the SENB specimens were examined using SEM. Figure 93a-c and Figure 94a and b show the SEM micrographs of the fracture surfaces of NCRSF SENB specimens containing 0.75 wt% and 1 wt% nanoclay, respectively. These two amounts of nanoclay content were studied in order to elucidate an explanation for the

*Nanoclay-Reinforced Syntactic Foam***Table 6.2: Relative increase in (specific) K_{Ic} and G_{Ic} for different fillers added to pure epoxy resin**

Amount of Filler	% Increase in K_{Ic}	% Increase in K_{Ic}/ρ	% Increase in G_{Ic}	% Increase in G_{Ic}/ρ
30 vol% BJO-093	37.43	84.82	211.94	319.51
30 vol% BJO-093 + 1wt% nanoclay	107.72	170.04	449.88	614.84
30 vol% BJO-093 + 2wt% nanoclay	93.63	143.60	352.37	469.11
1 wt% nanoclay ¹	21.43	19.96	39.53	37.85
2 wt% nanoclay ¹	64.29	60.37	193.02	186.03

¹ taken from [162]

large difference in fracture properties between these two nanoclay contents. The three characteristic fracture regions, namely pre-crack (A), process zone (B), and the fast fracture region (C), are clearly visible in Figure 93a. The pre-crack region is produced by tapping of a fresh razor blade into the pre-notch. According to [65], the process zone is of interest as it harbours the toughening mechanisms responsible for the material's fracture toughness. The amount of fracture toughness is often reflected in the surface roughness and size of the process zone. The fracture surface of the process zone of specimens containing 0.75 wt% nanoclay, as seen in Figure 93b is rough whereas the fracture surface of the fast fracture region, see Figure 93c, is relatively smooth. A smooth surface is associated with brittle behavior and does not contribute significantly to the overall composite toughness. According to Zerda et al. [111], the rough surface exhibits evidence

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(a)

(b)

Nanoclay-Reinforced Syntactic Foam

(c)

Figure 93: SEM images of the fracture surface of an SENB specimen of nanoclay reinforced syntactic foam containing 0.75 wt% nanoclay; (a) overall fracture surface, (b) crack initiation zone, (c) fast fracture zone. The black arrow indicates the direction of crack propagation.

for crack branching along the path length. As the clay content increases, the distance between regions of intercalated clay is reduced. The reduced distance between the intercalated clay particles causes the crack to follow a more tortuous path, either around or between regions of high clay content. Increased clay content leads to increased crack path deflection, causing increased surface roughness. Indeed, the fracture surface of the process zone of specimens containing 0.75 wt%, as shown in Figure 93a, is less rough compared to the fracture surface of specimens containing 1.0 wt% nanoclay, see Figure 94a.

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(a)

(b)

Figure 94: SEM images of the fracture surface of an SENB specimen of nanoclay reinforced syntactic foam containing 1.0 wt% nanoclay; (a) crack initiation zone (low magnification), (b) crack initiation zone (high magnification)

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Besides the difference in roughness of the fracture surfaces, the size of the process zone also plays a significant role in the contribution to the fracture toughness. It is obvious that the process zone for samples containing 0.75 wt% nanoclay, see Figure 93a, is much smaller than the process zone observed on the fracture surface of NCRSF specimens containing 1.0 wt% nanoclay, see Figure 94a. The larger the process zone, the more toughening events have taken place, the higher the fracture toughness of the composite. Indeed, the fracture toughness of specimens containing 1.0 wt% nanoclay is higher than specimens containing 0.75 wt% nanoclay.

Figure 93b and Figure 94b show the process zones of NCRSF specimens containing 0.75 and 1.0wt% nanoclay, respectively. In the process zones many potential toughening mechanisms are observed, i.e. step structures, matrix deformation, microcracks, clusters of nanoclay particles, and fractured and debonded microspheres. The step structures behind the microspheres and clusters of nanoclay are a result of the crack front bowing mechanism, first described by Lange [76]. Besides the typical step structures observed behind the microspheres, step structures also occur behind nanoclay agglomerates. Nanoclay agglomerates tend to be in the order of microns, acting more as a micron particle. For higher nanoclay content, the size of the agglomerates tends to grow. If the size of the agglomerate is in the order of microns, the agglomerate is able to resist and deflect the crack front. This behavior is clearly visible in Figure 94b, where significant step structures are visible behind the nanoclay agglomerates. Interestingly, the step structures behind the nanoclay particles seem to be interacting with the surrounding microspheres. A similar phenomenon is shown in Figure 95b. This kind of interaction

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between microspheres and nanoclay layers could be a potential evidence of the synergistic behavior between nanoclay and microspheres. Further, it is shown in Figure 95a and b that the size of the nanoclay cluster affects the size of the resulting step structures. The larger the size of the nanoclay clusters, the larger the step structures, and thus the higher the fracture energy. This could be a possible explanation for the higher toughness values for syntactic foam containing ≥ 1 wt% of nanoclay particles.

Besides step structures, multiple microcracks are observed in Figure 94b (indicated by white arrows). Observations of these microcracks are similar to those reported by Wang et al. [162]. According to [162] the presence of the microcracks implies that the clay layers act as stress concentrators, promoting the formation of a large number of microcracks upon loading of the sample, causing an increase in the size of the process zone.

Optical microscopy (OM) was performed to study the sub-surface damage in the crack process zone. The study allows for evaluation of the possible presence of micro-shear banding as reported by Lee and Yee [70]. Micro-shear banding has been reported as an important toughening mechanism in glass sphere reinforced polymers. Despite observing multiple specimens containing different amounts of nanoclay under the optical microscope, no micro shear banding can be seen under polarized light. Similar findings are reported by [162] for epoxy/clay nanocomposites. The author believes that the absence of micro-shear banding could be attributed to the relatively low content of nanoclay layers in combination with their random orientation. Further it is suggested by the

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(a)

(b)

Figure 95: Step structures behind clusters of nanoclay; (a) 1 micron cluster, (b) 20 microns cluster.

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Figure 96: Transmission optical micrograph showing the subsurface damage near the initiation crack area in nanoclay reinforced syntactic foam. The black arrow indicates the direction of crack propagation.

author that the system might behave in an elastic manner causing ‘healing’ of the crack, leaving no traces of microshear banding.

Transmission optical microscopy revealed another toughening mechanism, see Figure 96. The image, taken under crossed polarized light, clearly shows the presence of diffuse matrix shear yielded regions due to the debonding of the microspheres. Diffuse shear yielding is always found around the debonded matrix. Once a microsphere debonds from the matrix, a free surface will be generated, which is more vulnerable to plastic shear deformation.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Based on the results presented in this thesis report, it can be concluded that syntactic foam can be toughened. Each of the toughening approaches presented in this thesis report elicit positive results in terms of toughening of syntactic foam. The conclusions drawn for each approach will be given in the follow paragraphs.

7.1 Effect of the porosity

From the results presented, it can be concluded that the specific properties of syntactic foam depend on the types and volume fractions of microspheres utilized in the syntactic foam. Increase in microsphere density (K46 vs. K15) and the thickness-to-radius ratio led to an increase in specific tensile stiffness. The results for the tensile and flexural tests were comparable due to the fact that both types of tests exhibited the same failure mode. Both tests elicited a decreasing trend in specific strength with increasing filler content. A distinct trend in compressive behavior was noted in contrast to the tensile failure. The compression tests revealed the excellent compressive properties of syntactic foam and in particular the superior performance of K46 microspheres, giving rise to higher compressive yield strengths and moduli compared to K15 and phenolic microspheres.

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From the fracture toughness tests, it was concluded that all types of studied microspheres show a similar trend in the specific fracture toughness with increasing filler content. For lower filler content an increase in the specific fracture toughness was observed. The increase reached a maximum after which a decrease in the specific fracture toughness was seen. The change in behavior was attributed to a change in the dominant toughening mechanisms from filler stiffening, crack front bowing to excessive debonding. The usefulness of a combination of desired properties for syntactic foam such as light-weight high stiffness, high compression and high toughness was clearly demonstrated.

7.2 Effect of short carbon fibers

Concomitant strengthening and toughening can be accomplished using fiber reinforcement of syntactic foam. 3 wt% fiber- reinforcement increased the tensile strength, Young's modulus, plane strain fracture toughness, and critical energy release rate by 40, 115 and 95, and 90% respectively. Such property improvements are considered impressive in polymer composites. The improvement in properties is caused by the synergistic interactions of short carbon fibers with microballoons. Fractured and debonded fibers, leading to increased matrix plasticity, step structures and microsphere debonding are believed to be responsible for the increase in tensile and fracture properties.

A conjectural estimate of the total fracture toughness gives rise to a similar trend to the measured fracture toughness of the composites studied. The estimate included the contribution to the overall toughness by fiber debonding, stress redistribution, fiber pull-

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out, and the generation of new surfaces. The latter proved to be the highest contributor to the overall toughness.

It can be concluded that the variation in fiber length between 3 and 10 mm does not affect the tensile and fracture properties significantly. A simple estimate based on the well-known Kelly-Tyson model indicates the studied fiber lengths could plausibly exceed the critical fiber transfer length, l_{crit} . Besides the mechanical and fracture properties, the fiber content and fiber length do not affect the thermal properties of short fiber-reinforced syntactic foam.

7.3 Effect of nanoclay

A syntactic foam reinforced with mostly intercalated nanoclay layers was synthesized. Tensile test results showed that an introduction of 2 wt% of nanoclay led to a 13% reduction in the tensile strength of nanoclay-reinforced syntactic foam and increased the Young's modulus by 19.5%. The reduction in the tensile strength was attributed to the presence of voids and agglomeration of the nanoclay layers. The tensile properties of nanoclay reinforced syntactic foam were not as good as similar properties observed for short fiber reinforced syntactic foam. For the fracture behavior, a maximum in the fracture toughness, K_{Ic} , and critical energy release rate, G_{Ic} , was observed for specimens containing 1 wt% nanoclay. The toughening effect was attributed to toughening mechanisms previously observed for pristine syntactic foam, i.e. crack pinning, matrix deformation, and debonded microspheres. In to those mechanisms, the

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nanoclay layers introduced additional crack deflection and micro-cracking. The intensity of the crack deflection increased with the size of the nanoclay agglomerates.

Comparing the results to epoxy/clay nanocomposites, it can be concluded that nanoclay reinforced syntactic foam shows superior properties. The result confirms the synergistic behavior between nanoclay and microspheres. However, overall, micro-toughening proved to be more effective than nano-toughening.

7.4 Recommendations for future work

- A) For the current project, the short fiber reinforced syntactic foam (SFRSF) exhibited a random orientation of the short fibers. The random orientation was unavoidable due to the processing method. It is well known that superior properties are obtained for uni-directional orientated short fibers. The author recommends the design of a device which will allow for the alignment of the short fibers in the syntactic foam mixture. The author recommends the design of a die similar to the one sketched in Figure 97. A disc is pressed down, pushing the mixture of matrix, microspheres and short fibers through a die. Due to the shear force between the mixture and the die wall, alignment of the fibers is expected. Due to the nature of thermosetting resins, a die made of Teflon is advised.

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Figure 97: Recommended apparatus to achieve aligned short fibers in short fiber reinforced syntactic foam

- B) For the current project, commercially available short carbon fibers were used to enhance the fracture properties of syntactic foam. It would be interesting to repeat the studies with surface-treated fibers. Improvements in the mechanical and fracture properties are expected due to enhanced interaction between the matrix and the fibers.
- C) Most of the works reported on syntactic foams, including this thesis project, involve studies on the structural properties of syntactic foam. The author believes that the functional properties of syntactic foams deserve more attention as it could open up a whole new field of applications for syntactic foams. Functional properties of interest for aerospace and marine applications would be radar wave absorbance, EMI shielding, and thermal

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conductivity. Combining the structural and functional properties into one composite system would lead to additional structural weight savings in aerospace and marine structures. By using a multi-layered functionally graded syntactic foam system, the author recognizes that each layer can be tuned towards a certain performance, creating a system that can be operated at a wide range. The author sees potential in the further exploration of carbon/carbon syntactic foam.

- D) The author recognizes the importance of studies on the toughening effect of carbon nanotubes. In general, carbon nanotubes outperform the short carbon fibers. Based on the results presented in this report, the author believes that inclusion of carbon nanotubes in syntactic foam would lead to even better results. Besides improvement in the mechanical properties, the author expects that the incorporation of carbon nanotubes could also contribute to improved functional properties, like i.e. EMI shielding, radar wave absorbance, and thermal conductivity.

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APPENDIX A

LIST OF PUBLICATIONS

A.1 Refereed Journal Papers

1. E.M. Wouterson, F.Y.C. Boey, X. Hu, and S.-C. Wong, “Fracture and Impact Toughness of Syntactic Foam”, *Journal of Cellular Plastics*, Vol. 40, pp. 145-154, March 2004
2. E.M. Wouterson, F.Y.C. Boey, X. Hu, and S.-C. Wong, “Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures”, *Composites Science and Technology*, Vol 65, No. 11-12, p.1840-1850, 2005.
3. E.M. Wouterson, F.Y.C. Boey, X. Hu, S.-C. Wong. “Effect of Fiber Reinforcement on the Tensile, Fracture and Thermal properties of Syntactic Foam”. *Polymer*, Vol. 48, No. 11, p. 3183-3191, 2007.
4. E.M. Wouterson, F.Y.C. Boey, L. Chen, S.-C. Wong, X. Hu. “Nano-toughening vs. Micro-toughening of polymer syntactic foam”. *Composites Science and Technology*, Vol. 67, No. 14, p. 2924-2933, 2007.

A.2 Refereed Papers in Conference Proceedings

1. E. M. Wouterson, F.Y.C. Boey, X. Hu and S.-C. Wong “Fracture Toughness and Impact Resistance of Syntactic Foam” in Proceedings of the 61st Annual Technical Conference of the Society of Plastics Engineers, ANTEC 2003, v 2, p 1742-1746.
2. E. M. Wouterson, F.Y.C. Boey and S.-C. Wong “Fracture Toughness of Microsphere-reinforced Syntactic Foam” in Proceedings of 2003 SEM Annual Conference & Exposition on Experimental and Applied Mechanics, JUNE 2 - 4, 2003, Charlotte, North Carolina
3. E. M. Wouterson, F.Y.C. Boey, X. Hu and S.-C. Wong “A study on fracture toughness of syntactic foam” in the Proceedings of the ICMAT 2003 International Conference on Materials for Advanced Technologies (ICMAT 2003) Singapore International Convention & Exhibition Center, MRS Singapore
4. E.M. Wouterson, F.Y.C. Boey, X. Hu and S.-C. Wong “Specific Properties vs. Microstructures for Syntactic Foam” in Composite Technologies for 2020: Proceedings of the 4th Asian-Australasian Conference on Composite Materials ACCM-4, Part 2: Characterisation, June 2004, Sydney, Australia

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5. Erwin M. Wouterson, Freddy Y.C. Boey, Xiao Hu, Shing-Chung Wong. 'Effect of the filler content on the specific properties of syntactic foam' in Proceedings of Annual Technical Conference – ANTEC 2004, Volume 3: Special Areas, p 3176-3180.
6. F.Y.C. Boey, E.M. Wouterson, X. Hu, S.-C. Wong. 'Toughening of syntactic foam'. (Keynote Lecture). In proceedings of STEPI7, University Montpellier II, France, 2005.
7. E.M. Wouterson, F.Y.C. Boey, X. Hu and S.-C. Wong. 'Reinforced syntactic foam: the effect of fiber content on the tensile and fracture properties' submitted to Proceedings Symposium W - ICMAT 2005 International Conference on Materials for Advanced Technologies (ICMAT 2005) Singapore International Convention & Exhibition Center, MRS Singapore
8. E.M. Wouterson, S.-C. Wong, F.Y.C. Boey, X. Hu, and L. Chen. "Toughening of syntactic foam using nanoclay particles". in Proceedings of IMECE2005: ASME International Mechanical Engineering Congress, Orlando, FL, November 5-11, 2005
9. E.M. Wouterson, F.Y.C. Boey, X. Hu, S.-C. Wong. The effect of fiber content and fiber length on the tensile and fracture properties of short fiber-reinforced syntactic

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foam. In Proceedings of ACUN-5 “Developments in composites: Advanced, Infrastructural, Natural, and nano-composites”, p. 81-86, UNSW, Sydney, Australia, 11-14 July 2006.