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Author(s):	Keller, Jennie
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Jennie Keller
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Literature Review: An Overview of Epoxy Resin Syntactic Foams with Glass Microballoons

INTRODUCTION

Syntactic foams are an important category of composite materials that have abundant applications in a wide variety of fields. The bulk phase of syntactic foams is a three-part epoxy resin formulation that consists of a base resin, a curative (curing agent) and a modifier (diluent and/or accelerator) [12]. These thermoset materials [12] are used frequently for their thermal stability [9], low moisture absorption and high compressive strength [10]. The characteristic feature of a syntactic foam is a network of beads that forms pores within the epoxy matrix [3]. In this review, hollow glass beads (known as glass microballoons) are considered, however, solid beads or microballoons made from materials such as ceramic, polymer or metal can also be used [3M, Peter]. The network of hollow beads forms a closed-cell foam; the term closed-cell comes from the fact that the microspheres used in the resin matrix are completely closed and filled with gas (termed hollow). In contrast, the microspheres used in open-cell foams are either not completely closed or broken so that matrix material can fill the spheres [11]. Although closed foams have been found to possess higher densities than open cell foams, their rigid structures give them superior mechanical properties [12].

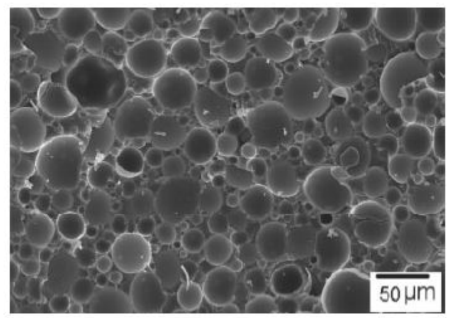

Figure 1: Microstructure of a syntactic foam containing 60% microballoons by volume [4]

Past research has extensively studied the effects that changing the volume fraction of microballoons to epoxy will have on the resulting syntactic foam [3,4,9]. In addition, published literature also explores how the microballoon wall thickness affects the final product [4,9,10]. Findings detail that indeed both the mechanical and some thermal properties of syntactic foams can be tailored to a specific application by varying either the volume fraction or the wall thickness of the microballoons used [10]. The major trends in syntactic foam research show that microballoon volume fraction has an inversely proportionate relationship to dynamic properties, while microballoon wall thickness is proportional to those same properties [3,4,9,10]. The glass transition temperature has a proportional relationship to the volume fraction of microballoons used, however, there is limited research that supports correlations between other thermal variables and microballoons specifications. In fact, very little experimental data exists to relate thermal conductivity and volume fraction or wall thickness of microballoons [5]. This review proposes that thermal conductivity should be a topic of interest for future researchers because of how frequently syntactic foams are used in insulating applications.

This paper will explore three aspects pertaining to epoxy resin syntactic foams with glass microballoons: the immense range of applications that syntactic foams are used for, the materials and fabrication techniques most commonly used, and lastly the results from characterization of syntactic foams with varying microballoon volume fractions and wall thicknesses. In addition to varying microballoon parameters, it is also possible to change the base, accelerator and curing agent used in the epoxy formulation. For simplicity, this paper will focus on a very common combination of materials produced by the Dow Chemical Company®.

APPLICATIONS OF SYNTACTIC FOAMS

In the paper *Applications of Polymer Matrix Syntactic Foams*, Gupta et al. writes "Syntactic foams have pushed the performance boundaries for composites and have enabled the development of vehicles for traveling to the deepest parts of the ocean and to other planets [7]." This displays precisely how significant the production of syntactic foams has become. In addition Salleh et al. explains how "[the] same chemistry, developed for aerospace applications, is now being used to produce lightweight bicycle frames, golf clubs, snowboards, racing cars, and musical instruments [12]." Because this class of composite materials can be tailored directly for a specific application, the possibilities of its usages are endless.

The development of the first syntactic foam dates back to the mid-1950s when a syntactic foam material consisting of hollow glass microspheres was produced for floatation of deep-submergence vehicles [2]. Today, "marine structures are still the primary application sector for syntactic foams [7]." This field uses syntactic foams for their high hydrostatic compressive strength, low moisture absorption, and high buoyancy [7]. The foams are incorporated in flaps and rudders of submarines, employed as fillers in ships, as structural agents in remotely operated vehicles (ROVs), human operated vehicles (HOVs), autonomous underwater vehicles (AUVs), buoys, and other oceanographic equipment platforms [7]. The Deepsea Challenger, under operation of James Cameron during his exploration of the Mariana Trench was made of reinforced syntactic foam [7]. In addition, the Hydroid REMUS 6000 AUVs used for the search and recovery expeditions of the Titanic, Amelia Earhart and the Air France 447 were made of ESS (Engineered Syntactic Systems) syntactic foams [7]. These applications require the material to endure tremendous pressure and must be able to withstand dimensional changes and resist moisture at all costs- syntactic foams have proven to be the greatest composite material for these purposes to date.

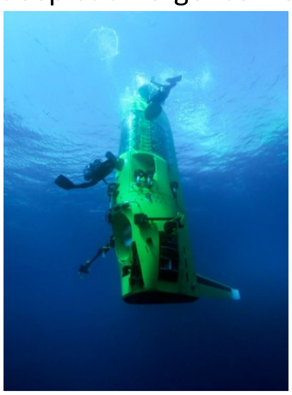

Figure 2: Deepsea Challenger used by James Cameron [8]

Many interesting applications of syntactic foams can be found in the aerospace industry. Some of the biggest names in aircraft such as Boeing and Airbus Americas use syntactic foams in the fabrication of their aircrafts [7]. These foams are employed as reinforcements within hollow areas of aircrafts, fillers for propellers and guide vanes, they enclose and protect electronic equipment and are widely used as potting materials to fill ends of structures [7]. In addition to military, commercial and private aircraft, syntactic foams are utilized in spacecraft structures as well. Largely, syntactic foams are incorporated as thermal insulators within spacecraft because of their very low coefficients of thermal expansion (CTE) [7]. They were utilized for insulation of the external fuel tank and rocket boosters of the United States Space Shuttle [7]. Overall, the aerospace industry benefits greatly from the advances of syntactic foams because of their low CTE [5], their low densities [4], and higher dimensional stability and load bearing capacities [9].

Recently, a popular function of syntactic foams has been in deep-sea oil pipelines and other applications in the oil and gas industry [5,7]. Because of their low densities, low moisture absorption [9] and low CTE, they are used for buoyancy and insulation [5,9]. In this situation, the closed-cell structure of the foams delivers the characteristics needed for these properties [9]. In addition to the gas and oil industry, syntactic foams are finding applications in sporting equipment as well as outdoor gear [4,7] where a lightweight composite material is needed [12]. Sporting goods such as bicycles, golf clubs, and snowboards are now being produced with syntactic foams as part of their structure [12]. Furthermore, one of the first applications of syntactic foams seen worldwide was in the soccer balls featured during the 2006 World Cup [7]. These balls were developed by Adidas to be lightweight and to regain their shape and size immediately after absorbing large amounts of force [7]. Syntactic foams are also being added to the structures of snow skis, archery bow limbs and baseball bats [7]. Other than sporting goods, everyday items such as furniture and food containers are made from syntactic foams, as well as radio equipment, and blast and fire protection devices [7]. The vast range of applications that uses syntactic foams support how valuable these materials have become in our advanced world.

MATERIALS AND FABRICATION OF SYNTACTIC FOAMS

Syntactic foams can be composed of a wide range of epoxy components, however, commonly referenced in literature are polymer matrix formulations using DGEBA based epoxy resin DER 332 and amine based hardener DEH 24, both manufactured by Dow Chemical® [4,7,9]. In addition to the matrix resin system, a diluent is typically incorporated to keep the viscosity of the resin-hardener system low during mixing [4]. The most widely referenced diluent is C_{12}-C_{14} aliphaticglycidylether [4,9,10]. For the sake of simplicity, this review will focus on syntactic foams made from these materials. According to Salleh et al., epoxy resins "offer high strength, low shrinkage, and excellent adhesion to various substrates, effective electrical insulation, chemical and solvent resistance, low cost, and low toxicity [12]." These are just some of the reasons that an epoxy matrix is used overwhelmingly in syntactic foams.

Most research conducted for epoxy-resin syntactic foams with glass microballoons uses a range of beads produced by 3M™ under the trade name Scotchlite [3,4,9,10]. 3M™ manufactures a wide range of glass microballoons that have a variety of different sizes, strengths, densities and compositions [12]. The microballoons utilized in the referenced literature were models S22, S32, S38, and K46 [4,9,10]. The true density of the bead is directly related to the wall thickness because the beads are hollow. Therefore, the K46 microballoon will have a larger density (ρ = 0.46 g/cc) as well as a greater wall thickness (ω = 1.29 μm) than the S22 (ρ = 0.22 g/cc and ω = 0.52 μm). Each bead has a variety of different applications and can be used to enhance certain aspects of a material. For example, the S32 bead can be used in an epoxy matrix to reduce the weight of the final product, reduce any volatile organic compounds within the material, and improve its water resistance [1]. Table 1 lists the densities, wall thicknesses and main enhancements of each of the four microballoons studied in this review.

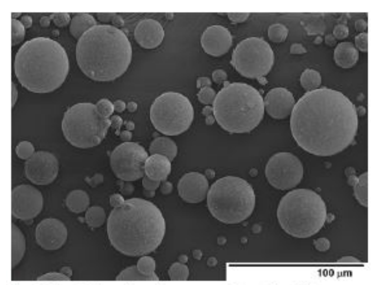

Figure 3: Glass hollow microspheres manufactured by 3M™ [7]

Table 1: Comparison of the Potential Enhancements of Each Microballoon Studied

	S22	S32	S38	K46
True Density (ρ)	0.22 g/cc	0.32 g/cc	0.38 g/cc	0.46 g/cc
Wall Thickness (ω)	0.52 μm	0.88 μm	1.05 μm	1.29 μm
Potential Enhancements:	Sandability/Machinability	Weight reduction	Weight reduction	Weight reduction
	Reduce shrinkage	Water resistance	Cost reduction	Resin displacement
	Thermal shock resistance	VOC reduction	Class A surface finish	Improved dimensional stability

Glass microballoons are examined in this review because they are the most common hollow microsphere material studied. They have a higher compressive strength than plastic microballoons and compared to traditional fillers such as talc or silica, glass microballoons have much lower densities [16]. The microballoons involved in the research within this review are widely analyzed and commercially available, which makes them an ideal choice for experimentation because there is reliable data on how the microballoons behave in comparable syntactic foams investigations.

A similar procedure is used for fabrication of glass microballoon filled syntactic foams throughout literature. All steps of the standard operating procedure are carried out at room temperature unless otherwise noted. The first step is forming the epoxy resin which consists of mixing the resin and hardener; if a diluent is used, the resin and diluent are combined first before adding the hardener. Next, the glass microballoons are added and mixed into a slurry before the mixture is cast into an aluminum mold and allowed to cure for 24-36 hours. Finally, the foams are post-cured at 100°C for three hours [3,4,9,10].

To fully understand syntactic foam structures, it is important to explain the microstructural aspect of porosity. There are two forms of porosity that occur within syntactic foams: microballoon porosity and matrix porosity [4]. Microballoon porosity is the air enclosed within the bead which is a controlled parameter and can be adjusted by selecting different bead densities [6]. Matrix porosity is air that becomes entrapped within the resin matrix between microballoons [6]. This is an undesirable form of porosity and greatly effects dynamic properties of syntactic foams [6]. There are several calculation methods that are used to estimate the total porosity in syntactic foams which can be found throughout literature. Some research represent syntactic foams as a three phased material consisting of the resin matrix, hollow particles and porosity, however, most available literature neglects the porosity phase and classifies the foams as simply a two-phase material [5].

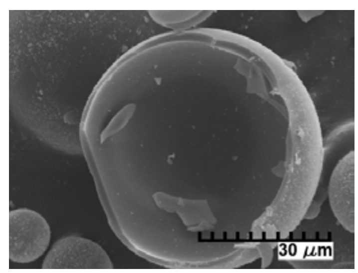

Figure 4: Broken glass microballoon showing thin wall and void space that was enclosed within the bead [4]

CHARACTERIZATION RESULTS AND DISCUSSION

Characterization of syntactic foams has led to correlations between microballoon properties (volume fraction, particle size, and wall thickness) and the thermal and dynamic properties of the resulting syntactic foams. The dynamic properties examined in this review are strength and modulus while the thermal properties considered are the glass transition temperature (T_g) and thermal conductivity. Very little experimental data is available to effectively relate conductivity to microballoon variables; however, a brief discussion of the theoretical models available is presented, along with the limited experimental results that help to predict the relationships between microballoon properties and thermal conductivity.

Compressive strength is an important parameter to characterize because it determines how much load a syntactic foam can handle before it fractures and breaks. Chen et al. analyzed the compressive strength of syntactic foams while varying the microballoon volume fractions of the K1 bead, 3M's lowest density microballoon [1,4]. This study focused on the effects of particle size and used three samples of syntactic foam with particle size distribution of 22.5–56 µm, 56–88 µm, and 92-125 µm. In addition to particle size, the volume fraction of microballoons was also varied. The analysis was performed using an Instron Series IX automated Material Testing System and applying ASTM D 695-96. Compression tests were conducting using a crosshead speed of 1.5 mm/min of 15 samples- five different volume fractions for each of the three particle distribution ranges. The results of this study were that as the volume fraction of microballoons increased in the syntactic foam samples, the compressive strength decreased. This behavior is the result of an increase in pores in the material, weakening the structure. Particle size distribution within the foams was found to have no effect on the compressive strength [4].

In addition to compressive strength, compressive modulus is another necessary parameter to know when designating a syntactic foam for a specific application. The modulus is the ratio of the stress applied to the material and the resulting compression of the foam. Comparatively, modulus is how much stress a sample can take without breaking while strength is the limit at which a sample is destroyed [13]. In a study published in the Journal of Engineering Materials and Technology, the effect of microballoon wall thickness on the compression strength and modulus of syntactic foams was considered [10]. The syntactic foams used a volume fraction of 60% microballoons but varied between the S22 and K46 bead. The compression testing used was a Split Hopkinson pressure bar apparatus for high strain rate testing. Three different strain rates were analyzed and the data transferred to a computer for calculation of modulus and strength via a stress vs. strain graph. The findings showed that as wall thickness increases, so do compressive modulus and strength. This is based on the idea that due to a higher wall thickness, a bead will possess larger crush strength and can ultimately sustain more loads thus increasing the strength and modulus of the overall syntactic foam [10].

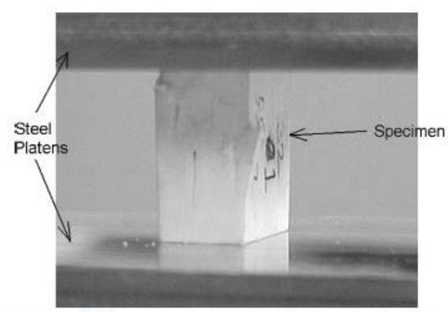

Figure 5: Compression testing of syntactic foam specimen using the Split-Hopkinson Pressure Bar (SHPB) technique [15]

Tensile strength and modulus are properties that are widely measured for materials used in structural applications such as syntactic foams. Tensile strength is the amount of force it takes to break a sample elastically while the tensile modulus is the amount of stress needed to stretch the sample a given distance [14]. Gupta et al. analyzed the effect of microballoon density and volume fraction on tensile strength and modulus [4]. In this study, low, medium and high-density microballoons were varied in syntactic foams at 30, 40, 50 and 60 percent. The microballoons used for this experiment were S22, S32, S38 and K46. At least five samples of each foam were tested and their outputs averaged. The method of testing used was an Instron

4467 Mechanical Testing System and an extensometer with 25 mm gauge length was used for data collection. Several trends were observed in this study and are summarized in figure 6.

No.	Sample name	Tensile strength (MPa)	Modulus (MPa)
1	SF220–30	17.6 ± 0.8	2,490 ± 197
2	SF220–40	14.2 ± 1.7	2,368 ± 218
3	SF220–50	12.4 ± 2.0	1,910 ± 145
4	SF220–60	11.0 ± 1.5	1,880 ± 61
5	SF320–30	19.2 ± 0.9	2,938 ± 80
6	SF320–40	19.0 ± 1.5	2,963 ± 118
7	SF320–50	14.1 ± 1.7	2,960 ± 173
8	SF320–60	13.6 ± 0.7	2,623 ± 205
9	SF380–30	23.2 ± 1.2	3,260 ± 106
10	SF380–40	20.2 ± 0.5	3,482 ± 218
11	SF380–50	14.6 ± 3.7	2,867 ± 67
12	SF380–60	14.1 ± 0.7	3,002 ± 53
13	SF460–30	25.1 ± 1.9	3,700 ± 126
14	SF460–40	20.7 ± 1.2	3,641 ± 121
15	SF460–50	15.6 ± 1.2	3,615 ± 190
16	SF460–60	12.8 ± 1.6	3,491 ± 99
17	Neat Resin	57.2 ± 2.6	2,752 ± 92

Figure 6: Tensile strength and modulus of syntactic foams [4]

Within each bead density, as volume fraction increased, the tensile strength of the syntactic foam decreased. Similar to results of compressive strength, the increase in volume fraction leads to a larger value of pores within the material, decreasing its strength. When comparing volume fractions of each density to one another, it was seen that the strength increased at higher bead densities. This is because the higher density beads have thicker particle walls and can sustain a larger value of force, ultimately delivering a higher value of strength. Similarly, the modulus values for increasing bead densities at the same volume fraction were also seen to increase. However, comparing the modulus values for the same bead density with different volume fractions, a consistent trend that applied to each density was not found. The results showed that the modulus decreased with increasing volume fraction for the low (S22) and high (K46) density beads, but not for the mid-density samples (S32 and S38) [4]. This outcome was unexpected and unexplainable by the researchers.

The glass transition temperature of a polymer is a crucial property to identify, especially when the material is used in applications that involve extreme temperatures such as insulation. Lin et al. explored how the thermal properties of syntactic foams are affected by microballoon density and volume fraction [9]. In this study, a similar array of samples was produced as in Gupta's *Tensile Properties of Glass Microballoon-Epoxy Resin Syntactic Foams* [4]. Low, medium and high density microballoons were varied in syntactic foams at 30, 40, 50 and 60 percent [9]. The microballoons used for this experiment were also S22, S32, S38 and K46. Thermal testing of the samples was done by DSC using a TA Instruments 2920. The dynamic mode of testing began by ramping the sample to 250°C at a rate of 20°C/min and then equilibrating. The samples were then cooled down to -10°C at a rate of 20°C/min and equilibrated. In the second heating cycle, the samples were heated back up to 250°C at a rate of 10°C/min. The results of this study show that as the volume fraction of microballoons increase, so does the T_g. This can be accredited to the increase in glass-content within the samples. At high volume fractions, the sample has a lower percentage of resin and a higher percentage of glass. This leads to the need for higher temperatures to change the physical state of the sample. In addition, the T_g values of syntactic foams with the same volume fraction but different bead densities showed no observable trend, indicating that the change in T_g is mainly due to the volume fraction of microballoons [9].

It is important to understand the effects of microballoon wall thickness and volume fraction on the thermal conductivity of syntactic foams because of the recent increase in use of syntactic foams as insulating materials [5]. However, in a review of thermal conductivity by Gupta et al., it is stated that "Experimental results are available for only a few compositions of syntactic foams. Basic understanding of the relationship between thermal conductivity of syntactic foams and the material parameters, such as hollow particle volume fraction and wall thickness, is not available through experimental results at this point." In addition, most of the theoretical models available for solid-particle-filled composites require modification to account for the porosity enclosed within the microballoons. Models such as the Liang Model, the Felske Model, the Pal Model and the Porfiri Model have been devised to predict the thermal conductivity of syntactic foams but can have limitations in that some deviate as volume fractions increase. However, in one study, the models were used in conjunction with experimental results of polypropylene matrix syntactic foams with glass microballoon. The experimental data was compared to theoretical results obtained from each of the four models. Interestingly, the experimental results matched very closely to those obtained theoretically. For this particular syntactic foam it was found that thermal conductivity of the decreased with increasing volume fraction of thin walled particles. In contrast, thermal conductivity decreased with decreasing volume fraction of thick-walled particles [5]. To solidify that this trend applies to all syntactic foams, it would be beneficial to do more thermal conductivity studies incorporating the theoretical models.

CONCLUSION

A review of scientific research focusing on the applications, fabrication and analysis of glass microballoon syntactic foams is presented. It is evident that the wide range of syntactic foam applications makes these composite materials incredibly valuable and important for many different industries.

The major trends of experimental studies are summarized in table 2.

Table 2: Effects of Varying Microballoon Volume Fraction and Wall Thickness on Syntactic Foams

	Increase Volume Fraction of Microballoons	**Increase Wall Thickness of Microballoons**
Compressive Strength	Decrease	Increase
Compressive Modulus	Decrease	Increase
Tensile Strength	Decrease	Increase
Tensile Modulus	Decrease	Increase
Tg	Increase	No effect
	Increase Volume Fraction of Thin-Walled Microballoons	**Increase Volume Fraction of Thick-Walled Microballoons**
Thermal Conductivity	Decrease	Increase

It has been found that a decrease in microballoon volume fraction will increase dynamic properties such as compressive strength, compressive modulus, tensile strength and tensile modulus [3,4,6,10]. The relationship between microballoon wall thickness and dynamic properties is seen to be proportional, where the thicker the microballoon wall, the higher the strength and moduli values [3,4,6,10]. In addition, studies have found that increasing the microballoon volume fraction will lead to an increase in the glass transition temperature of the syntactic foam, while varying the microballoon wall thickness had no observable effect [9]. It is proposed that more research be conducted to find reliable experimental data that supports the theoretical models for thermal conductivity.

The thermal and dynamic properties of syntactic foams play a crucial role in designing a material that has the combined thermal and mechanical properties required for a specific application. Desired properties such as thermal stability [9], low moisture absorption and high compressive strength [10] that make syntactic foams one of the most effective and valuable composite materials available today.

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