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Applications of Polymer Matrix Syntactic Foams

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A collection of applications of polymer matrix syntactic foams is presented in this article. Syntactic foams are lightweight porous composites that found their early applications in marine structures due to their naturally buoyant behavior and low moisture absorption. Their light weight has been beneficial in weight sensitive aerospace structures. 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. The high volume fraction of porosity in syntactic foams also enabled their applications in thermal insulation of pipelines in oil and gas industry. The possibility of tailoring the mechanical and thermal properties of syntactic foams through a combination of material selection, hollow particle volume fraction, and hollow particle wall thickness has helped in rapidly growing these applications. The low coefficient of thermal expansion and dimensional stability at high temperatures are now leading their use in electronic packaging, composite tooling, and thermoforming plug assists. Methods have been developed to tailor the mechanical and thermal properties of syntactic foams independent of each other over a wide range, which is a significant advantage over other traditional particulate and fibrous composites.

INTRODUCTION

One of the most promising aspects of composite materials is the possibility of structural weight reduction.[1] Polymer matrix composites can be designed to have a lower density at the same level of the mechanical properties as the bulk materials, which can lead to weight saving. All modes of transportation have explored the use of composite materials for structural weight reduction for various reasons. Aircraft weight reduction can result in increased flight range, cargo capacity, and speed, which can be useful for both military and civilian aircraft. Similarly, ground transportation vehicles and marine vessels can be made more fuel efficient and agile by structural weight reduction. Another benefit of weight reduction may be achieved by developing multifunctional materials that can incorporate more than one function in the same structure. Such opportunities have been made possible by composite materials.

Syntactic foams are a class of composite materials that are synthesized by dispersing hollow particle fillers in a matrix material.[2–5] These materials can be classified as both composite materials and foams. Although their development can be traced back more than 50 years, most of the research effort in these materials has taken place in the last 15 years. Some of the initial applications of syntactic foams were in marine structures due to the buoyancy obtained from their light weight. Methods have been developed in recent years to tailor the mechanical,[6–10] thermal,[11–13] and electrical properties of syntactic foams,[14,15] which have resulted in rapid increase in their applications. The current article summarizes the applications of syntactic foams with examples in a diverse range of fields.

MICROSTRUCTURE OF SYNTACTIC FOAMS

Syntactic foams are two-component composite materials containing hollow particles dispersed in a matrix. Hollow glass microspheres (HGMs) have been used widely in synthesizing syntactic foams.[16] An example of the commonly used 3 M Scotchlite Glass Bubbles (3 M, St. Paul, MN) is shown in Fig. 1. The hollow particles of a variety of ceramics and specialty materials are also commercially available now. An example of silicon carbide (SiC) hollow particles is presented in Fig. 2. Hollow particles of alumina, boron carbide, carbon, phenolic polymers, epoxy resin, and a variety of other materials have been used in syntactic foams.[17] Existing syntactic foams have used only spherical hollow particles. However, particles of a variety of shapes such as cubic, cuboidal, and cylindrical shapes are also available.[18]

The microstructure of syntactic foams is shown in Fig. 3, which represents an HGM-filled vinyl ester resin. The distribution of particles in the matrix resin is uniform. A solid model of syntactic foam microstructure is illustrated in Fig. 4. The closed cell structure of syntactic foams is useful in obtaining higher mechanical properties and lower moisture absorption compared to the open and closed cell foams containing gas porosity embedded in the matrix material.

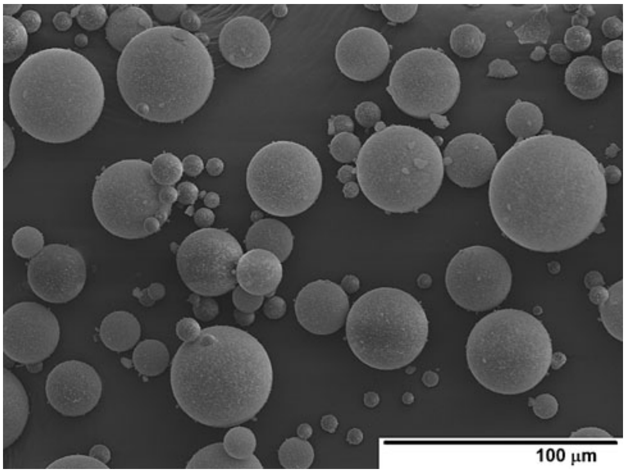

Fig. 1. Glass hollow microspheres manufactured by 3 M.

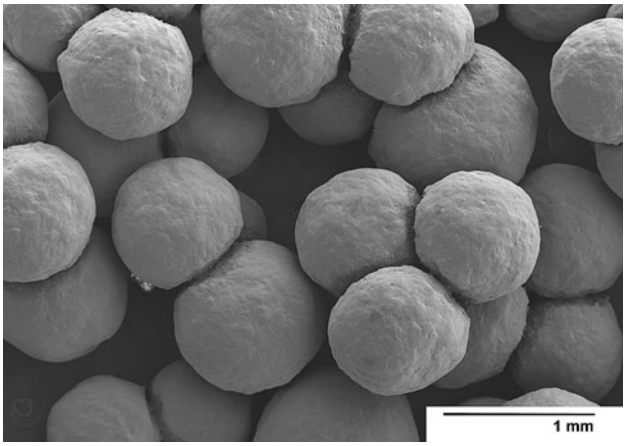

Fig. 2. SiC hollow particles manufactured by Deep Springs Technologies.

Generally, the particles used in syntactic foams have true particle density in the range 150 kg/m^3–800 kg/m^3, whereas the matrix materials have density in the range 1,000 kg/m^3–1,200 kg/m^3. The applications that are targeted toward weight-saving benefit from using lower density particles in high volume fraction. However, a balance between the particle volume fraction and wall thickness needs to be achieved to obtain the desired mechanical or thermal properties.

WEIGHT SAVING POTENTIAL IN STRUCTURES

Extensive experimental studies are now available on a variety of syntactic foams.[18–20] The data obtained from these studies have helped in validating theoretical models that can predict the mechanical and thermal properties of syntactic foams.[6,12,21] In solid particle-reinforced composites, the only parameter available for tailoring the properties of the composite is the particle volume fraction. Syntactic foams have particle wall thickness as an additional parameter that can be independently varied. The combination of these two parameters can provide some unique advantages in material selection in

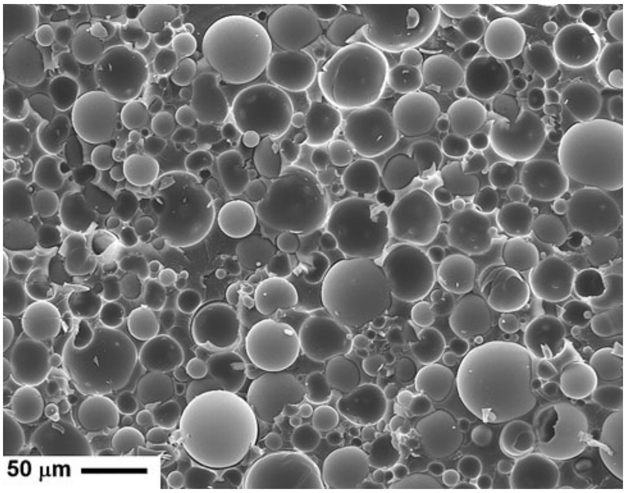

Fig. 3. Microstructure of a 60 vol.% hollow glass particle filled vinyl ester matrix syntactic foam.

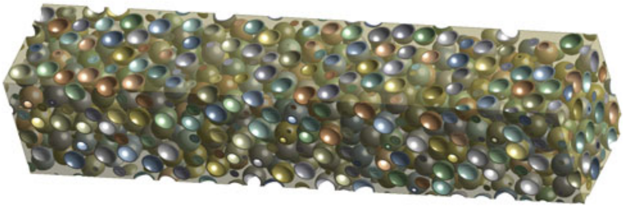

Fig. 4. Three-dimensional solid model representation of syntactic foams containing hollow particles. Image courtesy Dr. Dung D. Luong.

syntactic foams. An example is presented below for HGM-filled vinyl ester matrix syntactic foams. This example can be applied to electronic packaging applications of syntactic foams where the coefficient of thermal expansion (CTE) and modulus of the syntactic foams are important parameters. A similar approach can be taken for other properties as well.

The variation in the CTE for HGM-filled vinyl ester matrix syntactic foam system is calculated in Fig. 5a using a modified Turner's model developed in Ref. 12. The CTE (α) given by the modified Turner's model accounting for the wall thickness and the HGM volume fraction is given by

$$\alpha = \frac{\alpha_m \Phi_m E_m[(1-2v_g)+(\frac{1+v_g}{2})\eta^3] + \alpha_g \Phi_{mb} E_g (1-\eta^3)(1-2v_m)}{\Phi_m E_m[(1-2v_g)+(\frac{1+v_g}{2})\eta^3] + \Phi_{mb} E_g (1-\eta^3)(1-2v_m)} \tag{1}$$

where E_m and E_g are the modulus of the matrix resin and the glass, respectively; v_m and v_g are the Poisson's ratios of the matrix resin and the glass, respectively; and η is the ratio of inner radius to the outer radius of hollow particles and is called the radius ratio. The values of these parameters used in calculations for Fig. 5 are presented in Table I. The HGM density is varied between 100 kg/m^3 and 700 kg/m^3 through the change in the wall thickness for the same outer radius of particles and the HGM volume fraction (Φ_{mb}) is varied between 0% and 60% for the theoretical calculation.

The dashed line marked in Fig. 5a indicates all the compositions of syntactic foams that have the same CTE of 40 $\times$ 10^{-6}/°C. Similarly, as in another case, the dashed-dotted line marks the compositions that have the same CTE of 60 $\times$ 10^{-6}/°C. A theoretical model developed by Porfiri and Gupta[6] is used to obtain the syntactic foam modulus for the same range of HGM volume fraction and wall thickness and is shown in Fig. 5c. Furthermore, the density map of the syntactic foams having the same range of HGM volume fraction and wall thickness is developed using the rule of mixtures and is plotted in Fig. 5b. Because the variations of the CTE, modulus, and the density two-dimensional (2-D)

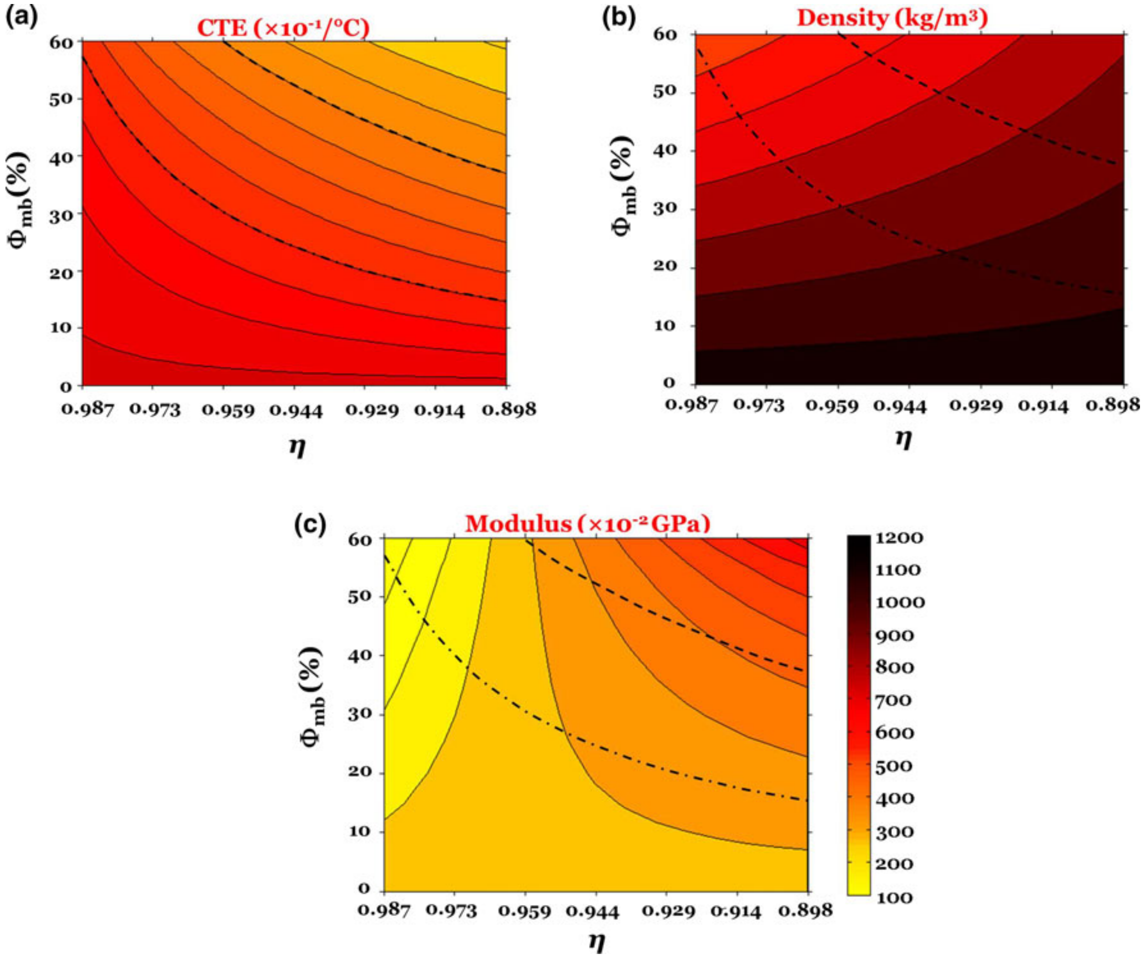

Fig. 5. Variation of the (a) CTE (μm/m/°C), (b) density (kg/m^3), and (c) modulus (GPa) of syntactic foams with respect to the HGM density and Φ_{mb}. The HGM density varies from 100 kg/m^3 to 770 kg/m^3 and the Φ_{mb} varies from 0 to 0.6. The scale in (*c*) is the cumulative representation of the CTE, density and modulus in their corresponding units. The *dashed* and the *dash-dotted lines* represent CTE values of 40 and 60 (μm/m/°C), respectively.

maps are based on the same rage of η and Φ_{mb}, these 2-D plots can be superimposed on each other to find the range of modulus and densities for the same values of CTE and the corresponding η and Φ_{mb} can be determined. Tables II and III provide the compositions, densities, and modulus of syntactic foams corresponding to the CTE values of 40 and 60×10^{-6}/°C, respectively.

Table 2 shows that the syntactic foams having densities in the range 644 kg/m^3–990 kg/m^3 can provide a CTE of 40×10^{-6}/°C. In this composition range, the modulus of syntactic foams varies between 2.8 and 4.1 GPa by changing the Φ_{mb} in the range 0.37–0.6 and correspondingly selecting appropriate η that ranges between 0.898 and 0.959. The second representative example for syntactic foams having a CTE of 60×10^{-6}/°C is presented in Table III, where the density ranges between 556 kg/m^3 and 1,091 kg/m^3 and the modulus ranges between 1.2 GPa and 3.2 GPa by tailoring the combination of η and Φ_{mb}. Depending on the requirements of an application, either syntactic foams of lowest density or desired modulus can be selected from this available composition range. This possibility of obtaining multifunctionality in the syntactic foam properties provides greater flexibility than solid reinforcement-filled composites.

The advantage of using syntactic foams in comparison to the neat resin, closed-cell air filled foams and solid particulate-reinforced composites is explained in Fig. 6. This figure includes results obtained from the same theoretical model and input parameters that are used for Fig. 5c. The addition of solid particles helps in achieving higher modulus values in comparison to the matrix resin at the cost of increasing the composite density. The addition of air pores, which creates closed-cell foams containing gas porosity, reduces the density while decreasing both modulus and specific modulus. In contrast, the addition of hollow particle fillers helps in decreasing the composite density while tuning modulus over a wide range based on the wall thickness and the amount of microballoon added to the composite. It can be observed in Fig. 6 that the modulus of syntactic foams can be significantly higher than the closed-cell foams at the same density level and the use of syntactic foams can lead to significant weight saving in structural applications. The combination of increased specific mechanical properties and decreased density allows for a reduction of the weight of a component while retaining the desired behavior. It should also be noted in this figure that the modulus of closed-cell foam is significantly lower than that of the matrix material, which is why their structural applications are scarce. A large number of compositions have a higher modulus than that of the matrix resin. Such compositions can find load-bearing structural applications.

Table I. Values of the parameters used in the current work[6,12]

Property	Value
ρ_m	1,160 kg/m^3
ρ_g	2,540 kg/m^3
E_m	2.82 GPa
E_g	60 GPa
ν_m	0.35
ν_g	0.21
α_m	76.5 μm/m/°C
α_g	4 μm/m/°C

Table II. Density and modulus of syntactic foams having a constant CTE value of 40 (μm/m/°C)

Φ_{mb} (%)	η	ρ_{mb} (kg/m^3)	ρ_c (kg/m^3)	E_c (GPa)
60	0.959	300	644	2.8
53	0.944	400	757	3.5
47	0.929	500	850	3.9
41	0.914	600	930	4.0
37	0.898	700	990	4.1

APPLICATIONS

The initial applications of syntactic foams were developed in marine structures where naturally buoyant behavior coupled with low moisture absorption and high hydrostatic compressive strength provided significant advantage over conventional foams. An increased understanding of the properties of these materials in the past two decades has enabled a variety of other applications. The thermal insulation properties of syntactic foams have been used in insulation for oil pipelines, along with other applications in the oil and gas industry. Two main differences exist in traditional solid reinforcement-filled composites and syntactic foams. The first difference is the availability of wall thickness as a parameter that can be modulated independent of volume fraction. This parameter has been found very useful in tailoring the mechanical properties. The second difference is the presence of air (or gas) in the particle cavity, which helps in tailoring the thermal properties of syntactic foams. A combination of these extended set of parameters has helped in tailoring the syntactic foam properties over a

Table III. Density and modulus of syntactic foams having a constant CTE value of 60 (μm/m/°C)

Φ_{mb} (%)	η	ρ_{mb} (kg/m^3)	ρ_c (kg/m^3)	E_c (GPa)
57	0.987	100	556	1.2
40	0.973	200	776	2.3
30	0.959	300	902	2.8
24	0.944	400	978	3.0
20	0.929	500	1,028	3.1
17	0.914	600	1,065	3.2
15	0.898	700	1,091	3.2

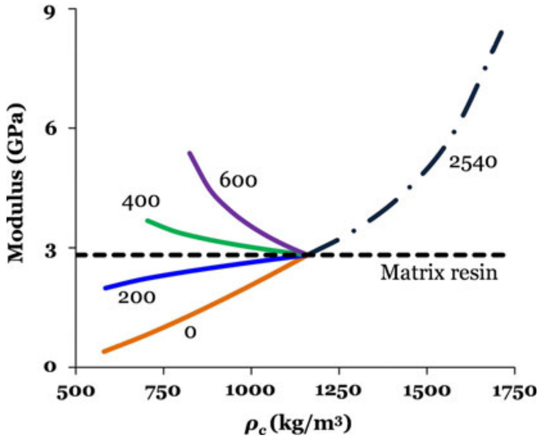

Fig. 6. Variation in the modulus with respect to density for syntactic foams. The *numbers* represent the density (in kg/m^3) of the reinforcing filler, where 0 represents air pores; 200,400 and 600 represent true particle densities of hollow glass microballoons; and 2,540 represents solid glass particles. The neat resin modulus is also included as the *horizontal dashed line* for comparison; the resin has density of 1,160 kg/m^3.

Fig. 7. HOV Alvin used for deep sea exploration. Photo courtesy NOAA.[22]

wide range and enable their applications. Examples of current applications are discussed in this section.

Marine

Marine structures are still the primary application sector for syntactic foams. Trelleborg Emerson & Cuming (TEC) and Trelleborg Offshore, Boston (TOB; Boston, MA) report the use of syntactic foam blocks in the forward and aft free-flood areas of submarines. BMTI ALCEN Group (Paris, France) reports the use of its syntactic foams in the rudders and flaps of submarines. Remotely operated vehicles (ROVs) and human-operated vehicles (HOVs) used in deep sea exploration have been constructed using syntactic foams. The Alvin HOV, shown in Fig. 7,[22] used for exploration of Titanic shipwreck and several other high-profile missions, used syntactic foam buoyancy aids. Alvin can go down to 4,500 m depth with three people onboard, and it has been operational since 1964. The Alvin HOV and the Jason ROV are used by the National Oceanic and Atmospheric Administration (NOAA) for underwater explorations. ROVs with syntactic foam buoyancy aids and structural components are used in the construction and maintenance of underwater pipelines. An example of such, the DeepOcean Supporter ROV, is shown in Fig. 8, which can operate up to the depth of 3,000 m and has a payload capacity of 350 kg. The Deepsea Challenger, used by James Cameron for the exploration of Mariana Trench, was made of reinforced syntactic foam containing fibers and hollow particles in an epoxy resin matrix. The syntactic foam was specifically designed for this submarine that went to the deepest part of the ocean. The syntactic foam structure of the Challenger craft during construction stages is shown in Fig. 9. The submarine and underwater vehicle structures require high hydrostatic compressive strength, low moisture absorption, and low density (for high buoyancy) in the material. In most cases, thermosetting resins are used as a matrix material with hollow glass particle fillers. Recent studies have shown that the soda-lime glass hollow particles can degrade in water.[23] The degradation occurs due to dealkalization and the degradation rate depends on the temperature. Alkali-free glass hollow particles are also available for use in such systems for longer term durability.

Fig. 8. DeepOcean Supporter ROV. Photo courtesy Ruth Clay, Trelleborg Offshore, Boston.

TEC also reports the use of their syntactic foams in eyebrows for 688 class U.S. nuclear submarines, such as USS Memphis shown in Fig. 10, [24] due to their buoyancy, acoustic profile and ability to significantly improve sonar functions. The control surfaces of these submarines were also filled with a variety of ultralight syntactic foams. TEC syntactic foams are used on submarines at Portsmouth Naval Shipyard. Utility Development Corporation (UDC; Livingston, NJ) reported the use of their syntactic foams in ROVs and autonomous underwater vehicles (AUVs), deep water moorings, torpedo targets,

Fig. 9. Deepsea challenger during construction stages with harnessed beam. Photo by Dianna Bisset.

Fig. 10. USS *Memphis* nuclear submarine, which uses syntactic foams in its control surfaces and fairwater planes.[24]

and sonar arrays. UDC also reported the use of their syntactic foams by NOAA in acoustic Doppler current profilers used in marine environments. Engineered syntactic systems (ESS) has reported the use of their syntactic foam fillers in ships and submarines at Point Loma, Norfolk Naval Shipyard, Northrop–Grumman at Newport News, Puget Sound Naval Shipyard, Kings Bay Shipyard, and at the Subsea Naval Base in Groton. ESS syntactic foams were also used in Hydroid REMUS 6000 AUVs (Hydroid LLC, Pocasset, MA) that were used in the Titanic, Amelia Earhart, and Air France 447 search and recovery expeditions. ESS reported use of over 3,500 cubic feet of their syntactic foams in the critical joint areas of the deckhouse of USS Zumwalt (DDG 1000) Guided Missile Destroyer. An image of the syntactic foam deckhouse is shown in Fig. 11.[25]

Fig. 11. Deckhouse of USS *Zumwalt* at Norfolk Naval Station.[25]

Syntactic foams supplied by ESS have been used on saturation diving bells for thermal and acoustic insulation. The added effect of buoyancy is another useful feature of these syntactic foams. Flotation modules for undersea pipelines manufactured by Flotation Technologies are shown in Fig. 12. Cuming Corporation reports producing syntactic foam buoyancy aids for deep sea drilling. Syntactic foams are also used as thermal insulation for undersea pipelines, as some components of heavy crude and hydrates in methane can solidify at undersea temperatures, clogging the line. UDC reported the use of its polyurethane-based syntactic foams as insulations for pipelines.

Most syntactic foam manufacturers report making buoys and other oceanographic equipment platforms. These applications require long life in surface or deep-water marine environments, where very harsh conditions are encountered. Some of the oceanographic equipment can be deployed to 8,000 m depth where tremendous pressure is encountered and compressive strength, dimensional changes, and resistance to moisture absorption are important requirements.

Aerospace

Aircraft

Boeing (Chicago, IL) and Airbus Americas (Herndon, VA) have both reported to use syntactic foams to reinforce hollow areas within the aircraft. TEC reports the use of syntactic foams (I) in jet aircraft radomes, rubstrips, and cowls as fillers for propellers and guide vanes, and (II) to encapsulate sensitive electronic equipment. In 2001, Boeing donated its patent for a type of syntactic foam used in the antenna units of the F/A-18E/F fighter jet (Fig. 13)[26] to the University of Pennsylvania, where the material was developed into a synthetic bone. The material was initially used by Boeing to

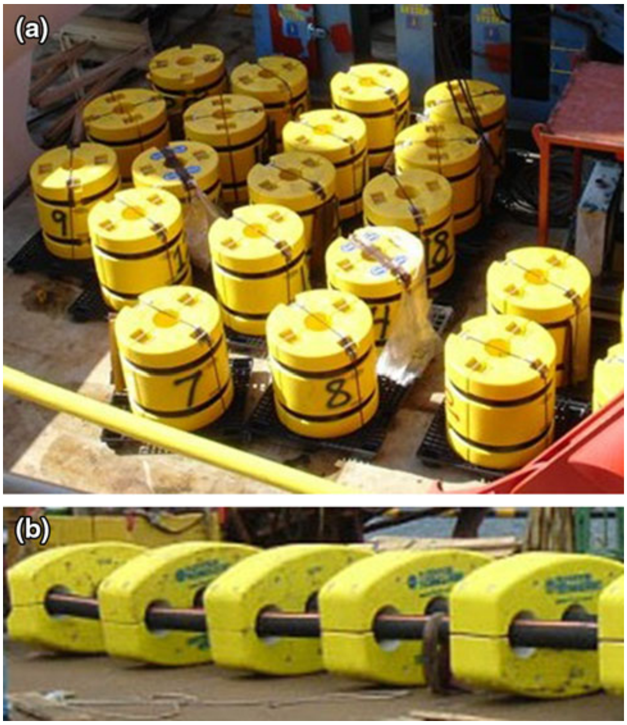

Fig. 12. Flotation modules used in marine applications: (a) a batch of modules and (b) flotation riser modules used for marine pipelines. Images courtesy: Peter Russell, Flotation Technologies.

encapsulate wing-mounted antennae without distorting radio signals. Boeing has also developed a syntactic foam called Microcell-SM foam, which combines glass HGMs with chopped fiberglass to achieve composite densities of 100 kg/m^3–300 kg/m^3. Applications also include potting materials used to fill the ends of honeycomb structures and sandwich material cores. Syntactic foams show numerous advantages over honeycombs, especially in the ability to create contoured surfaces and encapsulate radio equipment without interference.

Fig. 13. Boeing F/A-18E/F fighter jet, which uses syntactic foam to encapsulate radar equipment.[26]

Spacecraft Structures and Components

Thermal insulation properties of syntactic foams were used in space shuttle applications by the United States. Spray-on syntactic foams containing glass HGMs, chopped glass fiber, cork, and other inclusions were used as the insulation for the external fuel tank and solid rocket boosters on the Space Shuttle. Low CTE of syntactic foams has been useful in developing space mirrors that maintain dimensional stability during rapid and large temperature changes.[27] The Air Force Research Laboratory (AFRL) reported the use of carbon nanofibers and other nanomaterial-reinforced syntactic foams for space mirrors.[28] Cornerstone Research Group (Dayton, OH) worked with AFRL for developing these mirrors.[29] Zero or negative CTE can be achieved in syntactic foams, which is useful in avoiding geometrical distortion across temperature extremes. In addition, carbon nanofibers were used to obtain thermal conductivity in syntactic foams, which helped in eliminating temperature gradients and maintaining uniform temperature.

Consumer Products

Sports Equipment

One application of syntactic foams that gained worldwide fame was its utilization in adidas Fevernova soccer balls that were used in the 2006 World Cup. The technology, developed for this ball by Bayer and adidas (adidas America, Inc., Portland, OR), relied on a polyurethane syntactic foam. The syntactic foam layer helped in regaining the spherical shape of the ball immediately after being kicked, thereby enabling it to travel further and in the precise intended trajectory. In the tests by several top soccer players, this ball was considered to be the most precise soccer ball ever. Patents or reports are available citing the use of syntactic foams in snow skis,[30] archery bow limbs,[31] and baseball bats (for example: Easton WLA 110 Bbcor baseball bat).

Furniture

Saran microballoons composed of polyvinylidene chloride are mixed with epoxy or polyester to create a synthetic wood. The product has similar feel to real wood and is capable of accepting machine screws, nails, and staples. Saran microspheres are created as thermoplastic spheres filled with low-boiling-point hydrocarbons that are then boiled, increasing the particle size and drastically reducing particle density. The wall thickness of the expanded particles is 40 nm–50 nm.[32] Synthetic wood containing as little as 3 vol.% saran microspheres have density and compressive strength similar to birch.[33] Unlike natural wood, the compressive strength of birch is highly dependent on grain direction, whereas the composites are isotropic. Such synthetic woods are used in small boats and show high resistance to moisture exposure. Saran microspheres are also reported used in synthetic marble bathroom fixtures, including bathtubs.[34]

Food Containers

TOB produces the Eccolite product line, which is approved by the U.S. Food and Drug Administration for usage in food and beverage containers. Syntactic foams with thermoplastic matrices are capable of withstanding repeated thermoforming, allowing the containers to be recycled repeatedly.

Miscellaneous

Composite Tooling and Vacuum-Forming Plug Assists

Syntactic foams are used as composite material tooling boards and plug assists because of their thermal stability, low weight, low thermal conductivity, and easy machining. An example of TOB tooling board is shown in Fig. 14, where dimensional stability at higher temperatures is very useful. Low thermal conductivity is particularly important for plug assists because the primary cause of sheet sticking to the plug is localized cooling at the plug. An example of plug assists used by Tooling Technology LLC (Fort Loramie, OH) is shown in Fig. 15. TOB also has an Eccolite product line, which consists of thermoplastic matrix syntactic foams used as a plug assist, seen in Fig. 16. CMT Materials, Inc. (Attleboro, MA) produces a line of syntactic foams used as plug assists for thermoforming of plastic drinks containers and consumer goods packaging.

Radio Equipment

The radio transmission properties of syntactic foams are highly tailorable, which permits their use in a wide variety of radio systems. The British Aerospace Dynamics Group, U.K., has developed syntactic foam using quartz microspheres and epoxy or polyimide matrix for use in radomes for broadband microwave transmission. Syntactic foams can be made transparent to microwave radiation, which is useful in these applications because it protects sensitive equipment without distorting signals and can help military aircraft for stealth purposes. Precision Acoustics (Dorchester, UK) supplies syntactic foams for acoustic transducers. Conversely, syntactic foams that insulate microwave radiation are supplied by UDC.

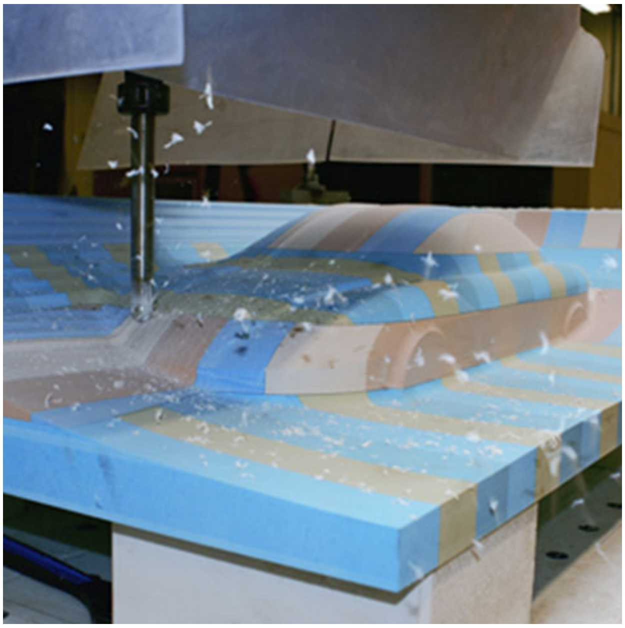

Fig. 14. Syntactic foam tooling board manufactured by Trelleborg Offshore, Boston. Image courtesy Ruth Clay.

Fig. 15. Syntactic foam plugs used in thermoforming process. Images courtesy Jeff Barker, Tooling Technology LLC.

Fig. 16. Eccolite Ultra syntactic foam plug assists used in thermoforming manufactured by Trelleborg Offshore. Image courtesy Ruth Clay.

Blast Protection

Trelleborg Offshore (Lancashire, UK) produces a line of syntactic foams used as blast protection for the undercarriage and doors of military vehicles. While metal shields can prevent damage to the vehicle, they may still transmit injurious shock waves to the occupants. Thus, syntactic foam shields are used for blast mitigation in conjunction with metal blast protection panels.

Fire Protection

XFlam (Melbourne, Australia) produces a flame-resistant, thermally insulating syntactic foam used in roofs, portable buildings, and refrigerated containers using a phenolic resin matrix. Trelleborg Offshore U.K. reports that the syntactic foams they produce for use as vehicle blast shields are also fire resistant. Some university-based research groups have also developed fire-resistant syntactic foams for use as core material in sandwich structures.[35]

SUMMARY

The examples show that a diverse set of applications exists for syntactic foams ranging from deep sea vehicles to space vehicles. Many missions, such as the Mariana Trench dive and space travel, have become possible largely due to the use syntactic foams that provided a combination of structural strength, light weight, and thermal insulation. It is found that the modulus of syntactic foams can be higher than that of the matrix resin, which enables their load bearing structural applications. It is also observed that the modulus of syntactic foams can be four-times higher than that of closed-cell foams containing gas porosity and having the same density value. The applications are expected to grow rapidly as the science and technology related to these materials continues to develop in the coming years. Theoretical models capable of predicting the modulus of syntactic foams accurately are now available. These models can help in identifying the parameters that can provide syntactic foams of desired properties as shown in the example for the CTE, modulus, and density. The availability of a wide variety of engineered hollow particles is also helping to grow the applications of syntactic foams in new sectors. Thermally conducting SiC hollow particles, high-strength alumina particles, and ultralightweight carbon hollow particles can lead to the development of specialty applications. Apart from structural applications using bulk quantities of syntactic foams, specialized applications such as electronic packaging, sports equipment, and acoustic transducers can provide value-added growth markets to syntactic foam manufacturers.

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