Effect of Short Fibers Reinforcement in Syntactic Foam: A Review

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Abstract. Syntactic foam is a low density but high compressive strength material. Insertion of fiber reinforcements has increased density of the syntactic foam. However, it has widened its application by the ability of properties tailoring with natural fibers. Influences of fiber length, fiber contents, types of fiber and slab orientation on properties have been reviewed in this paper. On the other hand, to reduce the dependence of high-cost microsphere, fiber reinforced macrosphere has introduced recently. “Rolling ball” and “electrostatic fiber flocking” methods found effectively to lower density and the latter method has better performance reserved. Yet no further information can be revealed currently. On the other hand, uneven properties of natural fibers were unfavored from the material selection. Nonetheless, it will be a “requirement” in future of composite materials innovation. This review paper served as a bird’s eye view for researchers to review the effect of fiber reinforcements in syntactic foams.

1. Introduction

Composite materials are widely used in many sectors due to high weight-to-strength ratio so that it can maintain performance but with lighter weight. Weight reduction in transportation section fuel saving, better payload capacity [1-6]. Besides, voids in composite materials provide significant contribution to weight reduction. However, it found limited applications due to deteriorated strength of composites. A branch of composite materials, syntactic foam, purposely filled with hollow particles in the matrix to create a low density material with minor compromising on mechanical properties. Syntactic foam is also categorized as particulate composites, porosity enclosed in thin stiff shells of hollow particles [7,8]. Syntactic foams exhibit promising compression performance with lower water absorption, dielectric contact as well as better thermal retardancy, responsible by the gas porosity embedded in the matrix [9]. These properties has made syntactic foams perfectly fits for floating devices [10], and buoyancy systems [11].

Insertion of filler reinforcements has increased the viscosity of mixtures and high volume fractions of hollow particles incorporation in this mixtures are prohibited, due to the high shear stress of mixing cause breakage of hollow particles [12]. Mixing in temperature higher than room temperature could
reduce the viscosity of mixture thereby higher volume of hollow particles is allowed. Another method to increase hollow particles volume fraction is the use of diluent.

Epoxy resin is the most popular matrix for syntactic foam, other than vinyl ester and phenolic resins, due to its high strength properties. As obeying the principle of composite materials, portions of syntactic foam materials can be tailored to produce an optimum performance for specific applications. Fillers like clay, fibers and particles can be used as reinforcements in syntactic foams to design an effective lightweight material. Enhancement of mechanical properties can be done by insertion of reinforcements into syntactic foams. However, dispersion of fillers or particles could be challenging especially nano-scale reinforcements tend to agglomerate. Microfibers can be easily dispersed by using mechanical stirring. On the other hand, nanoscale materials are often found mixing by using ultrasonic to avoid agglomeration [13,14].

The present of voids and porosities in syntactic foams led to density reduction. The porosity inside hollow particle are varied by different particle wall thicknesses, known as hollow particle porosity. Besides, entrapped air voids in the matrix during fabrication are known as matrix porosity. Most studies reported up 10 wt% of voids in syntactic foams [15,16]. The use of shaker during fabrication could reduce void contents effectively. However, void contents are not a major issue for compression applications as densification compacted the voids. Besides, closed-cell void structural does not increase moisture uptake significantly. In fact, matrix pores reduce density of syntactic foams, at the same time reducing mechanical properties and thermal stability.

Fiber reinforcements are found to enhance the properties of syntactic foam. Carbon fibers and glass fibers were the most popular reinforcements previously. However, natural fiber reinforcements are applied to reduce environment pollution impacts as well as properties improvement. On the other hand, insertion of microfibers also increased the density of composite, making it unflavored to many applications. Therefore, the limited volume fraction of fiber reinforcements is applicable in syntactic foams. Besides, nanofibers are the new trend of reinforcements in syntactic foam, which able to apply in lower volume with a larger contact surface area. Influence of several factors like fiber length, fiber content, types of fiber and slab orientation on mechanical and thermal properties has been reviewed in this paper and it served as a bird’s eye view for researchers to review the effect of fiber reinforcements in syntactic foams.

2. Fiber influences in fiber reinforced syntactic foam

2.1 Fiber contents

Insertion of high strength moduli fibers always reported in better strength performance. The scenario of fiber pullout and fiber debonding have caused less energy absorbed by composite, ended with lower strength loading [17]. Besides, entrapment of voids, poor compatibility between fiber and matrix resulted in early composite failure before reaching its maximum loading [18]. It is understanding that higher fiber contents insertion yielded higher syntactic foam density, consequently achieving better strength properties. Yu (2017), observed an increment of density with better strength when inserts 10 wt% of glass fibers into epoxy syntactic foam [19]. However, further addition of fibers has introduced crack initiation sites due to stress concentration, showing large deterioration in tensile strength but insignificant affected in compressive strength.

One study has reported significantly high void contents in glass fibers reinforced syntactic foam and resulted in lower composite’s modulus [20]. Clustering of fibers in syntactic foams is the main reason, where the fibers failed to disperse uniformly in matrix which hindered by microspheres (Figure 1). Hence, load transferring mechanism via fibers is not effectively as expected. On the other hand, agglomeration of carbon fibers also reported in previous study for syntactic foam [21]. For syntactic foam reinforced by 1phr carbon fiber, better flexural strength has been reported but this has decreased for higher fiber reinforcements. In low fiber contents, uniform distributed of fibers enhanced composite’s flexural strength. Besides, only small number of deformed microspheres have been found under flexural loading, showing microspheres is worked un-effectively for flexural properties [22,23].
On the contrary, high fiber contents act as stress concentration spots, causing decreases of flexural strength. Besides, Huang (2016), claimed that fiber orientations has a great influence on compression strength, as no significant differences found for compressive properties in random distributive short carbon fibers reinforced epoxy syntactic foam [21]. This has reported similar outcomes by Zhang (2013), observing microsphere debonding is the major action on compressive properties, while fibers and matrix play an insignificant secondary role [22]. The findings shown in figure 2.

Carbon nanofibers are useful in developing high performance composite due to their low cost and large surface area-to-low volume ratio [24,25]. A decrease in loss modulus observed in all type of carbon nanofibers reinforced syntactic foams. This may due to higher viscosity of foam after carbon nanofibers insertion, providing better bonding and hence greater modulus storage at whole temperature range. Besides, nano-scale fibers were observed in the air gaps and literately decrease void content into halve, which is less than 3% for all range of carbon nanofibers reinforcement compared to 5.2 vol% voids in plain syntactic foam [23]. Therefore, increment of carbon nanofibers found increases of storage modulus, and there is no report on fiber agglomeration when higher amount of nanofiber reinforcement being used [26]. On the other hand, glass transition temperature shows insignificant changes under presence of carbon nanofibers.

Figure 1: Clustering of fibers in epoxy syntactic foams [20].

Figure 2: Compressive strength of carbon nanofiber reinforced syntactic foam containing various amount of carbon nanofiber [22].

2.2 Fiber types

Insertion of short fiber reinforcements in syntactic foam has changed its load transferring mechanism. Karthikeyan (2000), discovered noticeable glass fiber pullout in less than 4wt% fiber reinforcement in epoxy syntactic foam, rather than resin binder fracture and resin/microspheres debonding or crushing of the microspheres, resulted in higher flexural strength values [27]. Relatively brittle epoxy syntactic foam shows a clear split of specimen under flexural testing while short fiber reinforced epoxy syntactic foams have bended appearance, giving evidence of enhanced flexural strength. However, inserts small amount of carbon fibers show significant improvement in stiffness, fracture toughness and impact properties yet glass fiber reinforcement almost no influences on epoxy syntactic foam. Besides, carbon fiber
reinforced epoxy syntactic foam shows greater adhesion and responsibility to better results yield for same fiber volume fraction [28].

On the other hand, 1 wt% of glass fiber reinforcement is more effective than carbon fiber insertion for minimize storage modulus reduction at room temperature compared to pure epoxy. However, additional carbon fibers in epoxy syntactic foam show better enhancement, yet overall reported lesser storage modulus and loss modulus [29]. Low thermal expansion coefficient is important to maintain dimensional stability in high temperature. Carbon nanofiber, CNF has gained much attraction for its promising thermal stability due to its nature, cup stacked structure with a hollow core. Each cup expanded in longitudinal and transverse direction under high temperature as figure 3 shown. Longitudinal cup expansion stacking in each other cups, literally reduced in longitudinal expansion. The study has found less than 27% deviation from modified Kerner’s model as compared to CNF insertion in epoxy syntactic foam [30]. The modified Kerner’s model and Turner’s model predictions of coefficient of thermal expansion listed in Table 1.

Poveda (2013), investigated the residual compressive properties after 6 month of moisture exposure and show in figure 4 [31]. Better compression modulus of CNF/epoxy composite found in wet condition due to the infused moisture filled up the voids appeared in composites. It is reported that moisture uptake of CNF reinforced syntactic foam is higher than CNF/epoxy composite. The water absorption was responsible to diffusion of water into microsphere cavities and progressively breaks down microsphere and lastly filled with water (Figure 5), resulted in lower modulus under wet condition. However, CNF insertion helped in retaining the modulus of syntactic foams. On the other hand, 6mm E-glass reinforced epoxy syntactic foam have immersed in 70°C water vapor, saline water and seawater. Water absorption contents found highest for water vapor immersion and it is identical to void contents, consequently reduces compressive strength. This is because massive ionic species presented in salt water are more difficult to diffuse into foam, while polar groups and hydrogen bonding of water molecules with high immersion temperature makes higher water vapor diffusion. Diffused water molecules hindering the interfacial bonding between matrix and microspheres as well as fibers, resulted in poor compressive strength.

Table 1: Modified Kerner’s model and Turner’s model predictions of coefficient of thermal expansion [30].

| Composite type | Turner’s model | Kerner’s model |
|----------------|----------------|----------------|
|                | α, x10⁻⁶°C | Δα, % | α, x10⁻⁶°C | Δα, % |
| N220-15-1      | 51.24      | 5.50  | 56.97      | 5.12  |
| N220-30-1      | 38.36      | 33.37 | 46.48      | 10.07 |
| N220-50-1      | 29.24      | 65.87 | 33.32      | 25.63 |
| N460-15-1      | 43.58      | 25.91 | 56.22      | 2.41  |
| N460-30-1      | 29.60      | 55.47 | 45.32      | 1.54  |
| N460-50-1      | 18.22      | 121.06| 32.05      | 25.66 |
| N220-15-2      | 51.84      | 1.48  | 56.14      | 6.29  |
| N220-30-2      | 39.59      | 33.46 | 45.81      | 15.33 |
| N460-15-2      | 44.61      | 10.56 | 55.39      | 10.95 |
| N460-30-2      | 30.93      | 35.78 | 44.66      | 5.97  |
| N220-15-5      | 46.69      | 6.36  | 50.36      | 1.40  |
| N220-30-5      | 35.84      | 45.30 | 41.17      | 26.49 |
| N460-15-5      | 40.29      | 31.77 | 49.69      | 6.85  |
| N460-30-5      | 28.13      | 51.13 | 40.13      | 5.94  |
| N220-15-10     | 46.30      | 3.61  | 48.87      | 1.84  |
| N460-15-10     | 40.53      | 18.87 | 47.07      | 0.22  |
Figure 3: Possible thermal expansion effects in carbon nanofibers [23].

Figure 4: Comparison of compressive modulus of moisture exposed and dry CNF/syntactic foams containing 1 wt% CNFs [31].

Figure 5: Degradation due to moisture can be seen in the GMBs [31].

2.3 Fiber Length
Short fiber reinforcement in syntactic foam shall enhance its performance, by introduce another load transfer mechanism by fiber on top of microsphere debonding mechanism. However, fiber agglomeration and higher voids content found at the same time. This has caused composite to be failed by cracking at concentration spot before it receives maximum load. Effective fiber length is a measurement to decide specific fiber length shall bring pros or cons to the system. With a simple estimation by using Kelly-Tyson model, critical fiber length, \( l_c \), that provide reinforcement to the system according to equation 1,

\[
l_c = \frac{d \sigma_f}{2 \tau_y}
\]

where, \( \sigma_f \) is the fiber strength, \( d \) is the fiber diameter, and \( \tau_y \) is assumed to be the matrix shear strength. Wounterson (2007), estimated in his research, 7μm diameter of carbon fiber reinforcement has a critical fiber length of 0.2mm [32]. All three lengths used in the study were exceeding critical fiber length. Therefore, it has found short carbon fiber improves strength of syntactic foam yet insignificant difference between three length of fiber reinforcements. Similar agreement from Nguyen (2010), has shown a close match between simulation results (1.380GPa) and experimental values for all the three
different fiber length reinforcements (1.41GPa, 1.53GPa and 1.66GPa for 3mm, 4.5mm and 10mm fiber length, respectively) [33].

2.4 Slab orientation
This review is reviewing previous works on short fiber reinforced syntactic foams. Generally, it is not possible to give control on fiber direction in the syntactic foams, since randomly orientation of short fiber insertion will always be found. However, syntactic foam slab is possible to stacks in positive and negative stacking (Figure 6). N-type foams showed similar value as neat syntactic foam [34]. A fascinating finding shows P-type slab orientation has dramatically increases all strength performance regardless of foam density (Table 2). The specimen has found initial crack propagated at 45° plane. This has agreed by Gupta (2002) study, cracking begins on one of corner and propagating to opposite corner, creating diagonal failure for high aspect ratio specimens (Figure 7) [35]. On the other hand, crack initiates on corner but a horizontal crack originates in the center region under compression loading for specimen less than 0.6 aspect ratio (Figure 8). Besides, varies of strength performance could be found also in single slab on different loading direction. As shown in SEM micrograph, applied load parallelly to fiber direction resulted found many uncrushed microspheres since the load carried out through the fibers. On the other hand, damaged microspheres observed for the load apply perpendicularly to the fiber reinforcements, resulted in lower compressive strength [36].

![Figure 6: Definition of N-type and P-type syntactic foams [34].](image1)

![Figure 7: Failure sequence of high aspect ratio syntactic foam specimens under compressive loading [35].](image2)
Figure 8: Failure sequence of low aspect ratio syntactic foam specimens under compressive loading [35].

Table 2: Mechanical testing for P-type and N-type short fiber reinforced syntactic foam slab [34].

| Density  | 250kg/m$^3$ | 300kg/m$^3$ | 350kg/m$^3$ |
|----------|-------------|-------------|-------------|
|          | Stress, MPa | Modulus, MPa | Stress, MPa | Modulus, MPa | Stress, MPa | Modulus, MPa |
| Sample   |             |             |             |             |             |             |
| Neat     | 1.87 ± 0.12 | 65 ± 5      | 2.83 ± 0.25 | 93 ± 6      | 4.55 ± 0.31 | 120 ± 11    |
| N-type   | 2.06 ± 0.18 | 70 ± 5      | 3.16 ± 0.26 | 89 ± 7      | 4.05 ± 0.27 | 120 ± 10    |
| P-type   | 4.80 ± 0.34 | 216 ± 19    | 6.27 ± 0.57 | 259 ± 23    | 8.33 ± 0.65 | 303 ± 27    |
|          |             |             |             |             |             |             |
| Neat     | 1.33 ± 0.11 | 140 ± 12    | 1.64 ± 0.13 | 160 ± 14    | 1.95 ± 0.16 | 184 ± 11    |
| N-type   | 1.01 ± 0.09 | 120 ± 11    | 1.06 ± 0.08 | 150 ± 13    | 1.18 ± 0.07 | 160 ± 14    |
| P-type   | 1.76 ± 0.12 | 188 ± 13    | 2.71 ± 0.22 | 262 ± 22    | 3.72 ± 0.22 | 395 ± 31    |
|          |             |             |             |             |             |             |
| Neat     | 2.32 ± 0.19 | 25 ± 2      | 2.35 ± 0.21 | 29 ± 3      | 2.38 ± 0.21 | 36 ± 4      |
| N-type   | 3.81 ± 0.28 | 31 ± 2      | 3.84 ± 0.34 | 31 ± 4      | 3.85 ± 0.33 | 31 ± 3      |
| P-type   | 4.85 ± 0.39 | 61 ± 5      | 5.34 ± 0.48 | 63 ± 6      | 5.94 ± 0.47 | 73 ± 8      |

3. Fiber powders reinforced macrospheres syntactic foams (FRMS)

Most studies are investigating largest filler contents in syntactic foam to observes maximum load capacity or lowest possible weight of composites. One method evolved from Samsudin method named rolling ball method, has prepared a different approach for three-phase syntactic foams [37]. Not much information being gathered since it is still an innovation idea. Current average fiber length used in rolling ball method processing is less than 0.7mm as compared to 6mm fibers used in ordinary reinforcement in syntactic foam [38].

In this method, fiber powders reinforcement was added onto resin-coated Expanded PolyStyrene (EPS) instead of just randomly dispersed in matrix, by using a tumbler of “rolling ball” coater machine. The rotating tumbler ensures uniform thickness of EPS coated beads. The coated EPS beads are then post-cured at temperature higher than melting point of polystyrene with intention of producing hollow structure within spheres. This fiber reinforced-hollow resin macrospheres shall use with microspheres in matrix to form a three-phase syntactic foam. The schematic process of “rolling ball” method and carbon fiber reinforced-hollow epoxy microsphere (CFR-HEMS) is shown in figure 9 and 10, respectively.

Wu (2016) has studied the relationship between the diameter of fiber reinforced macrospheres used with the density of composites. As expected, bigger diameter of macrospheres creates lower density of syntactic foams regardless of type of microspheres. The average epoxy foams are about 500-700kg/m$^3$, and higher density for ordinary fiber reinforcements. By utilized the empty space in macrospheres, density of the syntactic foams can reduce further to 450kg/m$^3$, at the same time retaining high compressive strength. Besides, this will cut down the dependence of high cost microspheres in low density syntactic foams, significantly reduced production cost [39].
Extra fiber coating layer on EPS beads was reported to brings higher performance profile and density [40]. The relationship between fiber coating layers with density is shown in figure 11. Increment of density was contributed by the thicker wall thickness of macrosphere and improves compressive strength. Fiber distributed uniformly in microsphere surface due to centrifugal force of rolling tumbler (Figure 12). It shall withstand high pressure to deform the macrospheres, evidenced from high compressive strength.

Besides, volume fraction of macrospheres is another crucial factor of determining density and strength. Wu (2015), concluded that 40% of macrospheres insertion is optimum parameter to gives higher compressive strength. Further addition of macrospheres reduce strength rapidly because direct contact between macrospheres was found reducing the compressive strength.

On the other hand, Yu (2018), has using newness idea, “electrostatic fiber flocking method” to fabricates macrosphere [38]. The authors claimed that this method could insert higher fiber contents on macrospheres, resulted in better strength performance. Besides, SEM micrograph (Figure 13) shows flocking method regularly arrange the fibers and perpendicularly to surface of EPS as compared to randomly arrangement of rolling ball method. Orderly arranged fibers allowed to transfer load effectively and increase maximum load capacity. However, this novelty method has no further studies by other researchers. Perhaps we can know more details of it in the future.
4. Future trend developments - Natural fiber reinforced syntactic foams

As responses to environmental, green materials are often substitute fully or partially in a product. Natural fibers are fibers that are obtained from living plants, animals or geological processes. It is one of the most important components used in green composite materials. Nevertheless, fewer studies done on natural fibers reinforced syntactic foams. Ghamsari (2016), claimed to be the first study on using natural sisal fibers in epoxy syntactic foams [41]. Low voids contents of natural fiber reinforced epoxy syntactic foams illustrating good fiber wetting and great adhesive properties. Evidence from lower maximum tan δ value of 3.5 wt% of sisal fibers reinforcements, displayed a better interfacial bonding. Furthermore, surface treatment on natural fibers shall expected to improve the bonding again.

Nevertheless, natural fibers reinforcement syntactic foam is unflavored by researchers because of uneven properties of the natural fibers makes composite’s properties tailoring harder [42]. Nonetheless, natural fibers insertion will be a “requirement” in future of composite materials innovation.

5. Conclusions

In the paper, influence of several factors like fiber length, fiber content, types of fiber and slab orientation on mechanical and thermal properties has been reviewed. Higher fiber contents have higher density of syntactic foam, consequently better strength properties will be achieved. However, excessed fiber contents introduced crack initiation sites due to stress concentration. Most of studies were using carbon or glass fibers reinforced in epoxy syntactic foams. This is because promising performance and matured development done on both fibers. Besides, CNF were applied to achieves better bonding between fibers and matrix. Low thermal expansion coefficient of CNF allowed to expand stacking in each other. Fiber length longer than critical length is important to enhance composite properties. Fibers shorter than the critical length will not carry their maximum load capacities thus unable to function effectively. Previous studies found agreed that fibers reinforcement longer than critical length has enhanced strength of syntactic foam. On the other hand, it is not possible to gives control on fiber direction in the syntactic foams, since randomly orientation of short fiber insertion will always be found. A fascinating finding shows P-type slab orientation has dramatically increases all strength performance regardless of foam density. Besides, damaged microspheres observed for the load apply perpendicularly to the fiber reinforcements (N-type), resulted in lower compressive strength. On the other hand, different compression failure mechanism observed for aspect ratio lesser than 0.6. “Ball Bearing” method for fiber powders reinforced microsphere has introduced to creates lower density syntactic foam with promising compression strength. The use of EPS was meant to reduce relies of high cost microsphere. Besides, “electrostatic fiber flocking method” creates fiber insertion directed perpendicular to EPS surface. This has dramatically increased the load transfer mechanism. However, no further information can be revealed currently. Lastly, natural fibers is one of the most important components used in green composite materials. Nevertheless, only few studies done on natural fibers reinforced syntactic foam.
Uneven properties of natural fibers were unflavored from material selection. Nonetheless, natural fibers insertion will be a “requirement” in future of composite materials innovation.

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