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Novel syntactic foams made of ceramic hollow micro-spheres and starch – theory, structure and properties

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Abstract

Novel syntactic foams made of starch and ceramic hollow micro-spheres were developed. Foams of four different micro-sphere size groups were manufactured with either pre- or post-mould gelatinisation process. Compressive failure behaviour and mechanical properties were evaluated. Not much difference in failure behaviour or in mechanical properties between the two processes (pre- and post-mould gel) was found. Compressive failure of all syntactic foams was of shear on plane inclined 45° to compressive loading direction. Compressive strength and modulus of syntactic foams were found to be dependant mainly on binder content but mostly independent of micro-sphere size. Some conditions of relativity arising from properties of constituents leading to the rule of mixtures relationships for compressive strength and to understanding of compressive/transitional failure behaviour were developed. The developed relationships based on the rule of mixtures were partially verified.

1. Introduction

Syntactic foams are particulate composites made of pre-formed hollow micro-spheres and binder. They can be used in various structural components. Compressive failure behaviour of syntactic foams has been studied by many researchers. Narkis et al[1,2] found that failure of syntactic foams with a low concentration of resin is mainly by disintegration under compression. It was reported, however, that a high density syntactic foam containing under compression failed with formation of 45° shear plane[3,4]. Recently Kim and Oh[5], and Gupta et al[6] have also reported that failure mode of a syntactic foam with relatively high concentration of resin under uniform compression was by shear on inclined planes. Gupta et al[6,7] highlighted that the shear failure mechanism is affected by specimen aspect ratio. Kim and Plubrai[8] studied low density (0.11 - 0.15 g/cc) glass/epoxy syntactic foams and found that compressive failure was of 'layered crushing'. Factors affecting the compressive failure behaviour, thus, may include various properties of constituents.

In this paper, new syntactic foams made of ceramic hollow micro-spheres and starch have been developed with a manufacturing method based on the principle of buoyancy[8,9,10]. Starch as binder for syntactic foams has not been employed in the past despite the fact that starch has some advantages over other binders such as epoxies, phenolics, etc in some applications. It is readily available, environmentally friendly, and an inexpensive renewable polymeric binder although it is dimensionally unstable during manufacturing. The ceramic hollow micro-spheres used for this paper is also inexpensive and available as part of fly ash from coal-fire power stations.

Also in this paper, mechanical behaviour of the novel foams under compression is studied for four different size groups of hollow micro-spheres and various starch contents within a newly proposed theoretical framework.

2. Development of rules of mixtures for syntactic foams

When binder content is too low, syntactic foams cannot be used as structural components. As it increases, however, syntactic foams become useful at some point and further their mechanical behaviour is affected by various conditions arising from relative properties of constituents and relativity between load carrying capacities of constituents.

The compressive load carrying capacity of syntactic foam (F_{sy}) is given by

$$F_{sy} = F_{ms} + F_b \quad (1)$$

where F_{ms} is the load carrying capacity of micro-spheres and F_b is the load carrying capacity of binder.

As volume fractions of constituents vary, two cases are possible i.e. $F_{ms} > F_b$ and $F_{ms} < F_b$.

The first case [$F_{ms} > F_b$] takes place when binder content is low so that micro-spheres take up more load than binder. However, as the binder content increases, the second case ($F_{ms} < F_b$) occurs so that a transition between the two cases occurs at a point where $F_{ms} = F_b$.

In the first case of [$F_{ms} > F_b$], bonding strength (σ_{bond}) between micro-spheres and binder in relation with micro-sphere compressive strength (σ_{ms}) or shear strength (σ^s_{ms}) depending on failure mode can be considered. Two different conditions are possible i.e. σ_{ms} (or σ^s_{ms}) $< \sigma_{bond}$ and σ_{ms} (or σ^s_{ms}) $> \sigma_{bond}$ as will be discussed below.

When the condition of [$F_{ms} > F_b$ and $\sigma_{ms} < \sigma_{bond}$] takes place, micro-spheres fail and subsequently binder fails because, when $F_{ms} > F_b$, binder alone is not capable of further resistance to an increasing compressive load. Failure behaviour in this case may be characterized by 'layered crashing' as details were already discussed elsewhere[8]. Another possible failure mode under the condition [$F_{ms} > F_b$ and $\sigma^s_{ms} < \sigma_{bond}$] is of shear. In this case, shear stress of binder ($\sigma^{s'}_b$) does not reach the shear strength of binder (σ^s_b) at the time microspheres fail so that $\sigma^{s'}_b < \sigma^s_b$. Shear failure surface would consist of shear failed broken micro-spheres and binder areas which are proportional to respective volume fractions (v_{ms} and v_b). Therefore, the rule of mixtures relationship for shear strength (σ^s_{sy}) and compressive strength (σ^c_{sy}) of syntactic foam can be obtained as:

$$\sigma^s_{sy} = \sigma^{s'}_b v_b + \sigma^s_{ms} v_{ms} \quad (2)$$

or

$$\sigma^c_{sy} = 2\sigma^{s'}_b v_b + 2\sigma^s_{ms} v_{ms} \text{ (for 45° shear plane)} \quad (3)$$

where, if shear strains of binder and micro-spheres (γ_b and γ_{ms} respectively) are equal at fracture (iso-strain condition),

$$\sigma^{s'}_b = G_b \gamma'_{ms} \quad (4)$$

where G_b is the shear modulus of binder and γ'_{ms} is the shear strain of micro-spheres at fracture.

When the condition of [$F_{ms} > F_b$ and or $\sigma^s_{ms} > \sigma_{bond}$] takes place, however, micro-spheres do not fail but debonding between binder and micro-spheres occurs. Once debonding occurred, binder alone is not capable of further resisting to an increasing compressive load, resulting in total failure of syntactic foam. Thus, fracture surfaces of syntactic foams consist of mainly unbroken micro-spheres. The compressive strength (σ^c_{sy}) of syntactic foams, therefore, is mainly dependant upon bond strength (σ_{bond}) particularly for a low binder content (generally dependant upon σ_{bond} and/or σ^s_b) but independent of strength of micro-spheres. When shear failure occurs, shear strength of syntactic foam (σ^s_{sy}) depends on debonding area (A_{bond}) which is larger than an ideally straight cut area of binder (A_{ideal}) inclined 45° to compressive loading direction. A_{ideal} is proportional to volume fraction of binder (v_b). Thus, it is not unreasonable to assume that debonding area is proportional to volume fraction of binder (v_b) to develop a rule of mixtures relationship for syntactic foam shear strength (σ^s_{sy}) given by

$$\sigma^s_{sy} = C' \sigma_{bond}\ v_b \quad (5)$$

or

$$\sigma_{sy}^{c} = C'C'' \ \sigma_{bond} \ v_b$$
$$= C \sigma_{bond} \ v_b \qquad (6)$$

where C' is a proportional constant, C'' is a constant (=2 for 45° shear) and C = $C' C''$.

In the second case of [$F_{ms} < F_b$] where volume fraction of binder is relatively high, the relativity between σ_{ms}^{s} and σ_{bond} is no longer of major issue in development of a rule of mixtures relationship for compressive/shear strength of syntactic foam because binder alone is capable of carrying load irrespective of bonding state even after failure of micro-spheres. Thus, relativity between fracture strains of micro-spheres and binder ($\gamma_{ms}^{'}$ and $\gamma_{b}^{'}$ respectively) appears to be appropriate to be considered for imposition of conditions (see below).

When the condition of [$F_{ms} < F_b$, $\gamma_{ms}^{'} < \gamma_{b}^{'}$] takes place, micro-spheres fail first on shear plane (if shear failure occurs) and then binder takes over the loading up to a point at which binder fails. In this case, the more micro-spheres the lower shear strength of syntactic foam for a given void volume fraction (v_v) until $F_{ms} = F_b$ if the iso-strain condition applies. The compressive strength of syntactic foam (σ_{sy}^{c}) therefore becomes

$$\sigma_{sy}^{s} = \sigma_{b}^{s} v_b = \sigma_{b}^{s} (1 - v_{ms} - v_v) \qquad (7)$$

or

$$\sigma_{sy}^{c} = 2\sigma_{b}^{s} v_b \quad (\text{if } \theta = 45°) \qquad (8)$$

where θ is the shear angle and v_v is for voids between microspheres (not within microspheres).

When the condition of [$F_{ms} < F_b$, $\gamma_{ms}^{'} > \gamma_{b}^{'}$] takes place, binder fails on shear plane first (if shear failure occurs) and immediately is followed by micro-sphere failure because micro-spheres alone are not capable of carrying further load. Therefore, micro-spheres contribute to the compressive strength of syntactic foam (σ_{sy}^{c}) but at a stress lower than its shear strength (σ_{ms}^{s}) so that, if the iso-strain condition applies,

$$\sigma_{sy}^{c} = 2\sigma_{b}^{s} v_b + 2\sigma_{ms}^{s'} v_{ms} . \qquad (9)$$

Note $\sigma_{ms}^{s'} < \sigma_{ms}^{s}$ and $\sigma_{ms}^{s'} = G_{ms}\gamma_{b}^{'}$ where G_{ms} is the shear modulus of micro-spheres.

Some example facture surfaces for $F_{ms} < F_b$, are found in the literature[5,6] although Equations (7) - (9) are subject to experimental verification.

Table 1 Particle size ranges and densities of ceramic micro-spheres employed**.**

Hollow micro-spheres	Size range (μm) (appox 95%)	Particle density (g/cc)	Bulk density (g/cc)
SL75	31 – 83	0.68	0.39
SL150	56 – 183	0.73	0.42
SL300	101 – 332	0.80	0.43
SL500	151 – 600	0.89	0.36

3. Constituent materials for manufacturing syntactic foams

3.1. Hollow micro-spheres

Ceramic hollow micro-spheres were supplied by Envirospheres Pty Ltd, Australia. Four different size groups (or commercial grades), SL75, SL150, SL300 and SL500, were employed and sizes were measured using a Malvern 2600C laser particle size analyser - results are listed in **Table 1**. Particle densities and bulk densities of the four hollow micro-sphere groups were also measured using an air comparison pycnometer (Beckman 930) and a measuring cylinder (capacity 250cc) respectively. Three hundred taps were conducted for each bulk density measurement. An average of five measurements was taken for each size group and is listed in **Table 1**.

3.2 Starch as binder

Potato starch (Tung Chun Soy & Canning Company, Hong Kong) was used as binder for hollow ceramic micro-spheres. Particle density of the potato starch was measured using an air comparison pycnometer (Beckman 930) and an average of three measurements was found to be 1.50g/cc. Bulk density was also measured using a measuring cylinder with a tapping device (300

taps were conducted) and an average of five measurements was found to be 0.85g/cc.

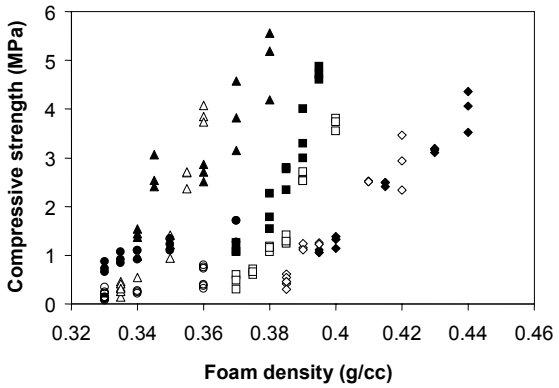

Figure 1 Compressive strength vs foam density: ▲, SL75 pre-mould gel; Δ, SL75 post-mould gel; ■, SL150 pre-mould gel; □, SL150 post-mould gel; ◆, SL300 pre-mould gel; ◇, SL300 post-mould gel; ●, SL500 pre-mould gel; and ○, SL500 post-mould gel.

4. Manufacturing of syntactic foams for compressive specimens

The basic principles of manufacturing for syntactic foams are given in references[9,10]. Various binder systems by varying starch concentration in water were prepared. Hollow micro-spheres (115 ± 35g) were added to the water-starch mixture placed in a transparent container (120 mm in diameter and 150 mm in height). The volume ratio of bulk micro-spheres to binder was approximately 1 to 3. The resulting mixture was manually shaken up after sealing for at least 90 seconds. The container was left for 5 minutes to allow for phase separation caused by buoyancy of micro-spheres. Top phase consisted of micro-spheres and binder, bottom phase binder and water as sediment, and middle phase water. The top phase was directly transferred using a scoop into a mould. Gelatinisation of starch in the mixture was conducted in two different ways of timing. One was prior to the addition of hollow micro-spheres to water-starch mixture and the other after moulding, which will be referred to as pre- and post-mould gelatinisation processes respectively. In the case of pre-mould gelatinisation process, the mixture of starch and water was heated until the gelatinisation fully occurred. The gelatinisation temperature range was measured to be 64-69ºC. Some extra amount of water was added in the starch-water mixture to maintain a constant ratio of starch to water during heating to compensate the loss of water due to evaporation. The mixture was cooled down to room temperature before moulding. Drying after moulding was conducted in an oven for 6 hours at 80°C and further 2 hours after demoulding. In the case of post-mould gelatinisation process, filled moulds were placed in an oven at the same temperature (80°C) for 1 hour with aluminium covers on to keep sufficient moisture/water in the mould for gelatinisation, and then for 5 hours without covers for drying in the mould and finally 2 hours further drying at the same temperature after demoulding.

5. Mechanical tests

Compression tests were conducted on a universal testing machine (Shimadzu 5000) with a Hounsfield compression cage at a crosshead speed of 1.0mm/min and at an ambient temperature range of 14–18°C. Platens of Hounsfield compression cage were lubricated using engine oil SAE 15-40 to minimise friction between specimen and each platen. Three samples were tested for each starch content in binder. They were compressed until about 20-50% of the initial height of the specimen, which was sufficient to observe the initial breakage and subsequent possible densification. Compressive strength was calculated using the original cross-sectional area.

6. Results and discussion

It was observed that compressive failure of all the foams is generally either by shear on planes inclined approximately 45^{O} to the loading direction or of 'cup and cone' type with vertical splitting. Not many broken micro-spheres were found on fracture surfaces of low binder contents, indicating that micro-spheres were mainly debonded and hence the failures were governed under the condition of [$F_{ms} > F_b$ and $\sigma^{s}_{ms} > \sigma_{bond}$]. In some other specimens of SL300 containing highest binder contents for both pre- and post-mould gelatinisation processes (prepared with a mass ratio of water to starch, 30/1), however, many broken micro-spheres were found on fracture surfaces, indicating the

condition of [F_{ms}> F_b and $\sigma_{ms}^{s} > \sigma_{bond}$] was terminated but the condition of [F_{ms}> F_b and $\sigma_{ms}^{s} < \sigma_{bond}$] commenced due to increased binder content. Note that binder content for all foams in this paper is still sufficiently low to be under the condition of F_{ms}> F_b.

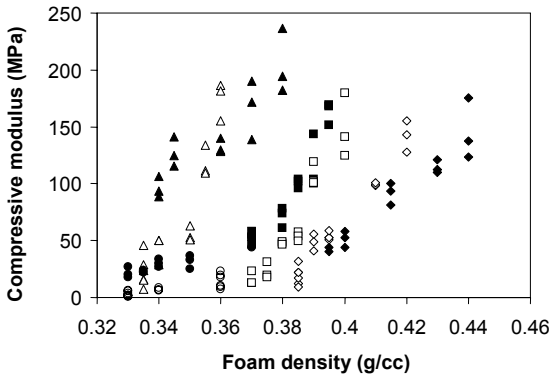

Figure 2 (a) Compressive modulus as function of foam density: ▲, SL75 pre-mould gelatinisation; Δ, SL75 post-mould gel; ■, SL150 pre-mould gel; □, SL150 post-mould gel; ◄►, SL300 pre-mould gel; ◇, SL300 post-mould gel; ●, SL500 pre-mould gel; and ○, SL500 post-mould gel.

Compressive strength (**Figure 1**) and modulus (**Figure 2**) of all the foams increase with increasing foam density as expected. They also increase as micro-sphere size decreases for a given density although SL500 displays some anomaly compared to others. Gelatinisation timing (pre- or post-mould), however, does not seem to affect much compressive strength and modulus for a given volume fraction of starch.

Compressive strength is replotted as a function of volume fraction of dried binder (or starch) and is given in **Figure 3**. In contrast to the previous plot in **Figure 1**, compressive strengths of SL75, SL150 and SL300 are seen to be approximately independent of micro-sphere size group as previously implied by the rule of mixtures equations. Now, the compressive strength of syntactic foams is directly affected by binder properties irrespective of compressive strength of micro-spheres under the condition of [F_{ms}> F_b and $\sigma_{ms}^{s} > \sigma_{bond}$] and hence Equation (5) or (6) can be employed. (Note that Equation (2) or (3) is not to be used because the condition of [F_{ms}> F_b and $\sigma_{ms} < \sigma_{bond}$] occurred at the end of the range as a result of increase in binder.) Equation (6) is plotted in **Figure 3** and its correlation coefficient was found to be 0.956 with 102MPa (= $C\sigma_{bond}$ in Equation (5)) for the three size groups (SL75, SL150 and SL300) collectively. SL500 micro-spheres were excluded in the collective analysis because they are somewhat different from other size groups of micro-spheres as observed. They are porous, of poor roundness and posses rough surface texture, possibly resulting in different bond strength (σ_{bond}) to other size groups of micro-spheres for a given binder content.

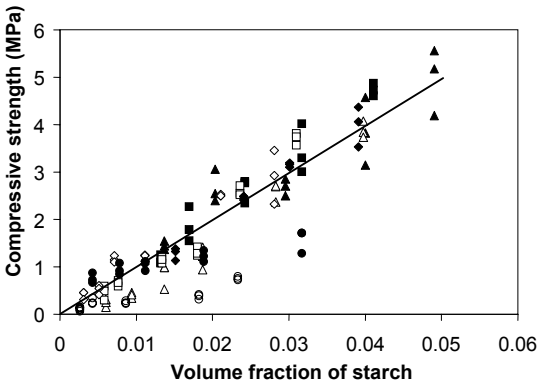

Figure 3 Compressive strength as function of volume fraction of starch in foam: ▲, SL75 pre-mould gelatinisation; Δ, SL75 post-mould gel; ■, SL150 pre-mould gel; □, SL150 post-mould gel; ◄►, SL300 pre-mould gel; ◇, SL300 post-mould gel; ●, SL500 pre-mould gel; and ○, SL500 post-mould gel. The least square line is for SL75, SL150 and SL300 collectively.

Compressive modulus as a function of binder content is given in **Figure 4**. Similarly to the compressive strength, it is mainly affected by binder content but not much by micro-sphere size. The least square line with a forced intercept at origin is plotted for the three sizes groups (SL75, SL150 and SL300) collectively and its correlation coefficient was found to be 0.937. SL500 was excluded again for the same reason as discussed for the compressive strength. Thus, the compressive modulus of three groups of micro-spheres (SL75, SL150 and SL300) appears to be approximately proportional to the binder content.

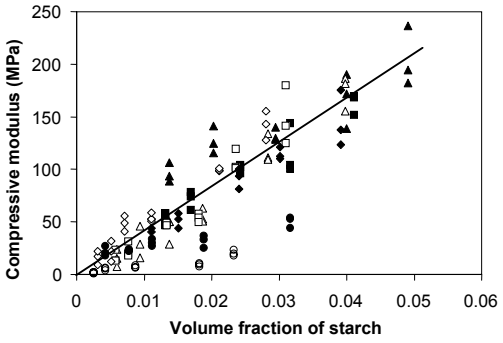

Figure 4 Compressive modulus vs volume fraction of starch in foam: ▲, SL75 pre-mould gel; Δ, SL75 post-mould gel; ■, SL150 pre-mould gel; □, SL150 post-mould gel; ◆, SL300 pre-mould gel; ◇, SL300 post-mould gel; ●, SL500 pre-mould gel; and ○, SL500 post-mould gel. The least square line is for SL75, SL150 and SL300 collectively.

7. Conclusions

Novel syntactic foams composed of hollow ceramic micro-spheres, starch, and voids have been developed. Various parameters such as micro-sphere size, volume fraction, and gelatinisation timing have been investigated for failure behaviour and mechanical properties of the syntactic foams. Compressive failure of all foams was found to be mainly by shear. Some conditions leading to the rule of mixture relationships have been developed for understanding of failure behaviour and compressive/shear strength. The developed rule of mixture relationships for compressive/shear strength were partially verified. It was found that compressive strength and modulus were not much affected by micro-sphere size and gelatinisation timing.

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