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Three-phase syntactic foams: structure-property relationships

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This study addresses a unique problem that occurs in composite materials containing hollow reinforcements, that is the density-filler content relationship. Unlike a traditional solid reinforcement, a hollow reinforcement can be manufactured with a variety of densities. Subsequently, when fabricating composite materials with a particular density requirement, a large variation in volume percent of that reinforcing phase can occur. Hollow reinforcements under consideration are carbon microballoons (CMBs) of various densities determined by both tap density and pycnometry. Our approach is to study several different densities and volume percents of microballoons while maintaining a constant volume percent (8.5%) of the polymer binder phase. The resulting syntactic foams are three-phase materials consisting of binder, microballoon (MB), and interstitial void phases. The volume of the MB and binder phase is measured by helium pycnometry. The complementary volume of the interstitial void phase will depend on the volume of microballoons in the billet. Mechanical characterization is done by compression and flexure testing and results are discussed to highlight structure-property relationships. Results show that, in addition to bulk density of the foam, the packing arrangement of the CMBs is an important factor in the mechanical behavior of the foam and is shown to be an important design criterion.

1. Introduction

A syntactic foam is a composite material containing hollow particles dispersed in a binder phase. This field of materials began to mature in the late 1960s and early 1970s. The largest application was and still is in marine and submarine sectors. Others are core materials in sandwich structures and aerospace applications [1].

The sizes of particles can range from nanometer to millimeter. When the hollow particles are in the micrometer-size range they are commonly referred to as microballoons (MBs). Many types of hollow particles have been used in syntactic foams, however, glass MBs are the most prevalent in research and applications.

There are two basic types of syntactic foams [1–3], three- and two-phase. A three-phase syntactic foam contains hollow particles and binder phase but not a sufficient binder volume to fill the interstitial positions between particles. The three phases being: MB (wall material and contained void), binder, and interstitial void. A two-phase material contains hollow particles and enough matrix material to fill these interstices. In this case, since the volume in-between the MBs is filled with material, the only phases are MB and matrix.

The most common syntactic foams are two-phase materials; for example, glass MBs in an epoxy matrix. This study, however, focuses on a different type of hollow particles, carbon microballoons (CMBs) as a component in a three-phase structure. Three-phase foams are of interest because of the very low density and therefore high specific properties and the ability to tailor foam density and MB and binder volume percent. Carbon has several properties that make it more appealing than glass in certain applications, specifically higher thermal and electrical conductivity and most alluring is the lower density. Carbon is

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also used in high temperature applications [4, 5]. Knowing that hollow reinforcements can be manufactured with a range of densities this paper addresses the issue of how CMB's physical structure affects mechanical properties. For example, a CMB can be manufactured with a bulk density ranging from less than 0.10 g/cm^3 to over 0.20 g/cm^3. The physical difference between the two being the higher density material will, on average, have a larger wall thickness to diameter ratio (t/d). When manufacturing a syntactic foam with a particular density requirement (constant mass of binder and MB per unit volume) the volume percent of the MB phase will vary significantly over the mentioned range. It is reasonable to postulate that the mechanical properties of these syntactic foams will also change even though the overall density and mass ratios of constituents remain constant. The packing arrangement of the spheres would seem to be an important factor in material behavior.

There have been studies on packing of spheres in two-phase syntactic foams [6–10]. Three of these [7, 9, 10] investigated mechanical properties as a function of both volume percent and MB density (wall thickness). The situation in these two-phase foams is an exchange of MB volume with matrix volume. Increasing the volume percent of the MB phase reduces the volume percent of the binder phase, which in-turn, varies the foam density, mass ratio, MB volume percent and matrix volume percent simultaneously.

This paper focuses on three-phase foams. Unlike the situation in two-phase foams, there is an extra degree of freedom in their manufacture. We choose to hold the binder phase constant at 8.5 volume percent. By doing so, and by using different densities of MBs, foam density can be constant while holding mass ratio constant and evaluating the effect of MB volume percent on syntactic foam properties. Essentially, we decouple mass percentages and constituent volume percentages at discrete foam densities.

For all foams in this paper, the CMBs are bonded together by 8.5 vol% percent bismaleamid (BMI) binder phase leaving the interstitial void as open-cell. We hesitate to refer to this as a matrix material since it does not meet the traditional definition, that of being a continuous phase. This paper will investigate how changing the following physical properties of three-phase syntactic foam:

1. CMB volume percent,
2. CMB density,
3. interstitial void, and
4. foam density

affect the compressive and flexure behavior of the syntactic foam.

2. Materials and procedure

2.1. Carbon microballoons and CMB Characterization

The precursor material for the CMBs are phenolic MBs manufactured by Asia Pacific Microspheres under the tradename Phenoset. The carbonization is done by Honeywell-Aircraft Landing Systems in South Bend, IN. The exact carbonization cycle is proprietary having a unique heat cycle with specialized equipment. Several patents are pending.

We have developed [11] a simple relationship between the bulk or tap density of phenolic and carbon material over the range of material in this study as:

$$\rho_{CMB,tap} \cong \rho_{PMB,tap} + 0.015$$

Two batches of CMBs were used in this study, having tap density of 0.179 and 0.138 g/cm^3 hereto referred to as high and low density CMBs, respectively.

The primary technique used to quantitatively compare different batches of CMB was tap density, ρ_{tap}, as per ASTM standard B 527 [12]. Briefly, the test procedure is to load a known mass of CMBs into a graduated cylinder and place the cylinder on a tapping apparatus. This equipment allows the materials to fall a predetermined distance 3000 times. The mass divided by the settled volume of the particles after the 3000 "taps" is the tap density. Particle density was another particle characterization technique and determined by using a helium Ultrapycnometer manufactured by Holimetrix Corp.

The ratio of the tap density to the particle density is the particle-packing factor (PF) or volume percent of the unbroken CMB in the tapped density packing arrangement. This number should be constant across all densities of CMB with the following assumptions:

1. particle density does not affect the settling properties,
2. friction between particles does not change, and
3. percentage of broken CMB does not change.

On average, across several densities of CMBs, PF achieved during tap density testing is approximately 0.38. A floatation test is routinely performed on all densities of CMBs and consistently less that 2% of the material sink. This gives an indication that the amount of broken CMBs is very low.

2.2. APO-BMI

The binder in this syntactic foam is a member of the class of materials called a bismaleamid (BMI). BMIs are a type of thermosetting polymer. Cross-linking can occur by several mechanisms but most common are by homopolymerization across the maleimide double bonds or by Michael addition chain extension reaction across these bonds.

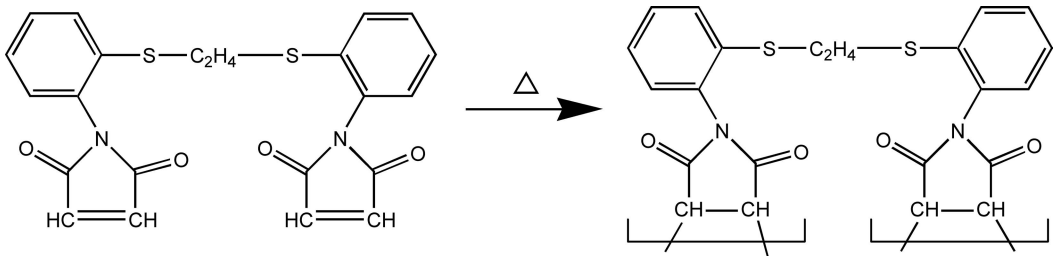

Figure 1 Shown is the chemical structure and polymerization mechanism of the binder phase, APO-BMI.

APO-BMI, the binder material used in this study, is manufactured by Honeywell FM&T in Kansas City, Missouri; the chemical structure and polymerization reaction of which are shown in Fig. 1. This single component, amorphous, thermosetting resin is a solid (powder) in the uncured state at room temperature. The thermal behavior of the material is very complex but in general, heating the material to $\sim 130^{\circ}$C will cause melting and further heating to 210°C will initiate the homopolymerization of the maleimide bonds. This large window between polymer melt and cross-linking allows for a unique processing procedure that is outlined in the following section.

The mechanical properties of the pure APO-BMI material are difficult to ascertain because of the problem in fabricating test specimens. The only mechanical property measured directly on the APO-BMI is the modulus at room temperature. It was determined to be 6.4 GPa using a nanoindentor.

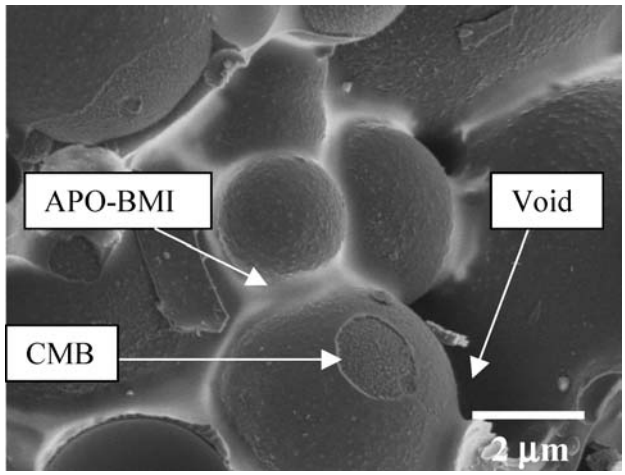

Figure 2 SEM micrograph of the syntactic foam structure showing the 3-phases: CMB, APO-BMI, and interstitial void.

2.3. Syntactic foam construction

Since APO-BMI is a solid at room temperature it was mechanically mixed in a V-shell mixer with the CMBs to make the molding compound. All syntactic foam billets were molded to contain 8.5% by volume binder. The mass and volume percents of the CMBs were varied and based on the tap density of each lot and the target density of the final foam.

As discussed earlier, the packing arrangement obtained during tap density testing is assumed constant across all densities of CMB. When this arrangement is reproduced in a billet of syntactic foam it will be hereto referred to as the "tapped density" condition. The packing arrangement can be altered by the addition or subtraction of a volume percentage of CMB from the tapped density condition, referred to as "overpacking." Billets were made at the –10%, 0% (tapped density), + 10% and + 20% etc. Overpacking is possible by the lubrication provided when the APO-BMI melts and is further aided by the application of external pressure when closing the mold. Mechanical packing of a mono-modal distribution of spherical particles is possible up to a packing factor (PF) of 68–70%. Beyond this point significant breakage occurs.

After placing the appropriate amounts of APO-BMI and CMBs in the V-shell mixer the two constituents were mixed for 60 min. This molding compound was then loaded into a 127 × 127 × 25.4 mm stainless steel mold. To first melt the APO-BMI, the mold containing the molding compound was placed in an oven and heated to 145° at a rate of 2°C/min. Sixty minutes after reaching 145°C the mold was removed from the oven, pressed to achieve the mold volume, and the top of the mold secured with screws. The mold was then returned to the oven, the temperature ramped to 225°C, and remained there for 4 hrs to cure the APO-BMI.

The resulting material was a three-phase syntactic foam, with constituents of CMBs, APO-BMI and interstitial void, as shown in the scanning electron microscope (SEM) image in Fig. 2 As mentioned, the APO-BMI had a constant volume percent of 8.5% while the volume percent of CMB and interstitial void made up the remaining 91.5%.

We would like to emphasize the distinction drawn between "interstitial void" located between adjacent CMBs and the "contained void" of a CMB. Following the established syntactic foam convention, interstitial void is a separate phase. Contained void along with the carbon of the MB wall make up another single phase of the CMB. At a given foam density the sum of these void volumes is constant, however, these two types of void are not considered equivalent. One focus of this paper can be thought of as

exchanging one type of void for the other and measuring the effect by mechanical testing.

2.4. Syntactic foam characterization

2.4.1. Mechanical characterization

Compression and flexure mechanical test specimens were machined from each of the 127 × 127 × 25.4 mm syntactic foam billets. Mechanical testing was performed on an Instron machine equipped with an LVDT for strain measurement.

Flexure specimens were machined to nominal dimensions of 4 × 10 × 125 mm. Testing was done in three-point flexure as per ASTM D5943 [13]. Compression specimens were machined to nominal diameter of 26.1 mm and height of 25.4 mm and testing done as per ASTM D695 [14].

2.4.2. Physical characterization

Both bulk and solid densities for all compression and flexure samples were determined in this study. A bulk density was calculated by mass determination and volume calculated by specimen dimensions.

Since the interstitial void is 100% open porosity the solid volume (MB + APO-BMI) was determined in a gas pycnometer. From these measurements and the fact the 8.5 vol% of APO-BMI was constant throughout this study, subsequent calculations of solid volume percent and CMB volume percent were done for each compression and flexure specimen tested.

3. Results and discussion

3.1. Compression testing

Fig. 3 is a sample plot of the compressive stress-strain curve for the syntactic foam material under study. It exhibits typical composite behavior having a linear elastic loading section followed by a plateau region and graceful failure. The portion of the curve labeled "fast crack propagation" in Fig. 3 is the point at which a crack propagates perpendicular to the applied load through the entire specimen and is accompanied by audible sound. After this point, if the load were removed, the sample would be in at least 2 pieces. During compression testing however, the material can continue to load beyond this point. In light of this, the compression strength of the material is defined as the maximum strength attained before the point of fast crack propagation. Fig. 4 is an SEM micrograph of a fracture surface that failed in compression. It shows visual indication of both CMB and APO-BMI fracture as failure mode, which is consistent with other published works on three-phase foams [15, 16].

Fig. 5 plots compression strength as a function of CMB volume percent for samples containing CMBs of 0.179 and 0.138 g/cm^3 tap density. Looking at both sets of data individually indicates the compression strength increases with increasing volume percent of CMBs; not surprising

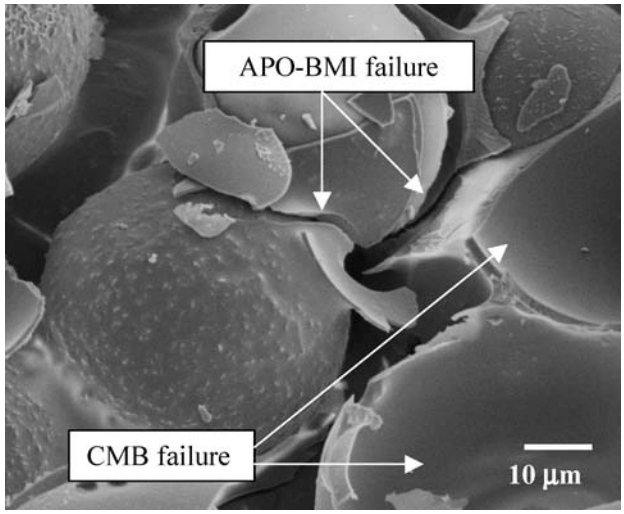

Figure 4 An SEM micrograph showing a syntactic foam fracture surface that failed in compression, it exhibits evidence of both binder and CMB failure.

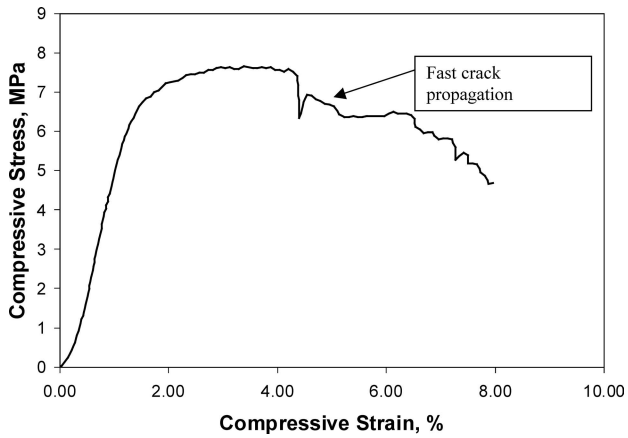

Figure 3 Typical compressive stress-strain behavior of this syntactic foam.

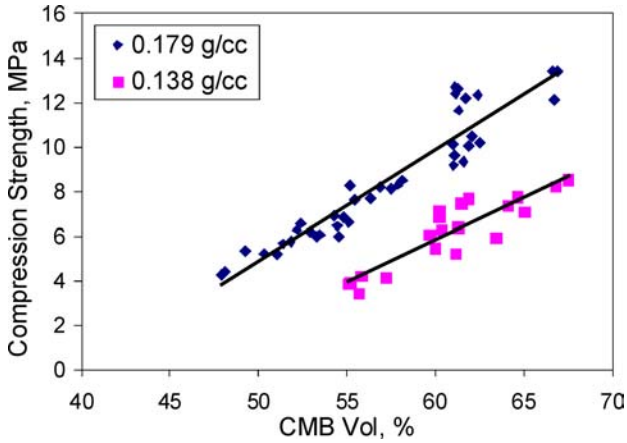

Figure 5 Compression strength data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

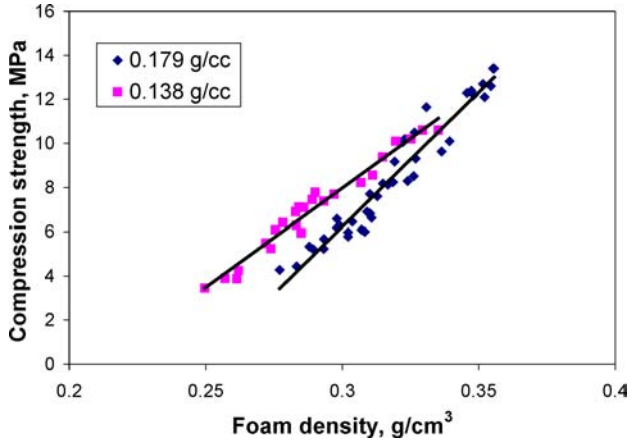

Figure 6 Compression strength vs. foam bulk density data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

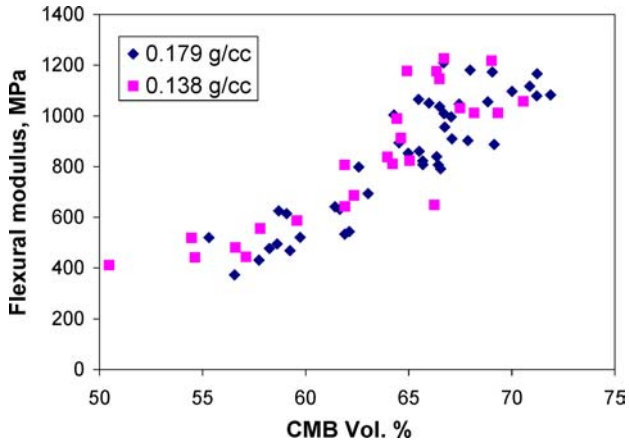

Figure 7 Compression modulus data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

since the net result of overpacking is an increase in foam density.

Comparison between the data sets shows that at a constant volume percent, the high density CMBs produce a stronger syntactic foam. We have shown through single MB compression testing that the higher tap density CMBs have a higher average strength and wall thickness [17–19]. These are stronger MBs thus produce a stronger foam at a given volume percent. This is arguably another obvious outcome except when plotted as compression strength vs. foam density as in Fig. 6. If it were solely a function of bulk foam density then the results obtained from the two densities on CMB should superimpose. However, as shown in Fig. 6, in the range of a bulk density between 0.26 to 0.32 g/cm^3 the foam made from the low density CMBs is stronger; from $\sim$50% stronger at 0.28 g/cm^3 to $\sim$15% stronger at 0.32 g/cm^3. This is significant since at a given density, the mass ratio of binder and CMB is constant; the only difference being how the carbon is distributed. The lower density CMBs will have a higher packing factor at a particular density than the high density CMBs. So the arrangement of the carbon, i.e. PF, is an important characteristic in understanding the compression behavior of this foam.

The same trends discussed above in the strength data are seen in the compression modulus data contained in Figs 7 and 8.

Summarizing, the compression behavior is not only dependent on the bulk foam density (carbon and APO-BMI), it is also dependent on the volume percent occupied by the CMBs and the density of CMB. The CMB PF, thus the interstitial void volume, is an important characteristic in understanding the compressive behavior of this type of foam.

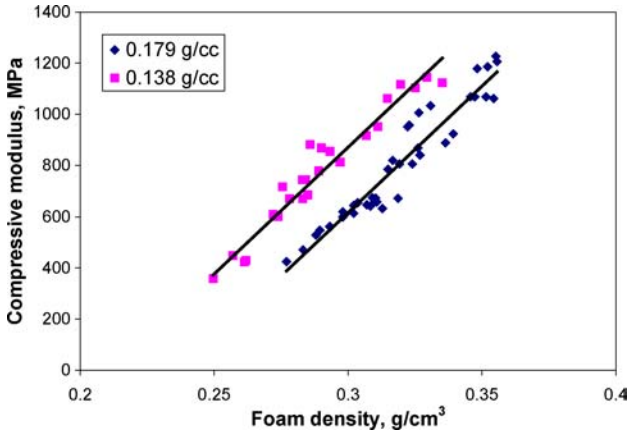

Figure 8 Compression modulus data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

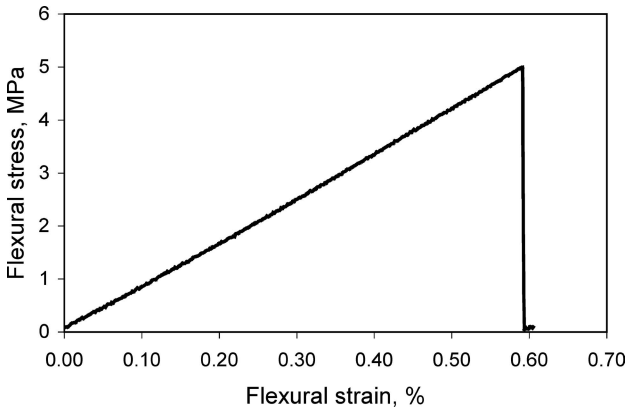

Figure 9 Typical stress-strain curve of this syntactic foam in a 3-point bend configuration.

3.2. Flexure testing

Fig. 9 is a sample plot of the flexure stress-strain curve for syntactic foam material under study. It shows a brittle failure consisting of a linear elastic loading curve followed by catastrophic failure at a relatively low strain, always less than 0.7%. Failure initiates on the tensile side of the three-point bend specimen. Fig. 10 is an SEM micrograph of a fracture surface showing that the interfacial failure between the CMB and APO-BMI as being the primary failure mechanism.

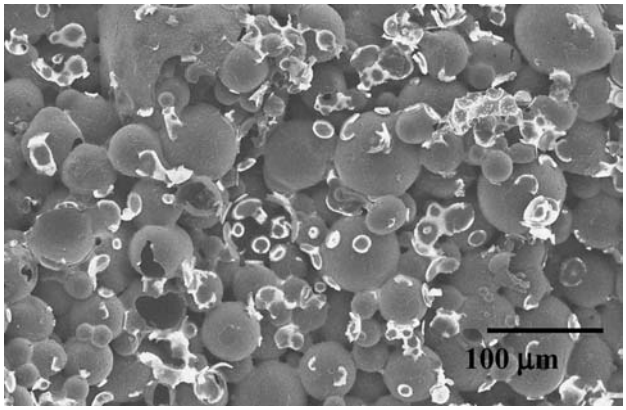

Figure 10 SEM micrograph showing the interfacial failure between the APO-BMI and CMB.

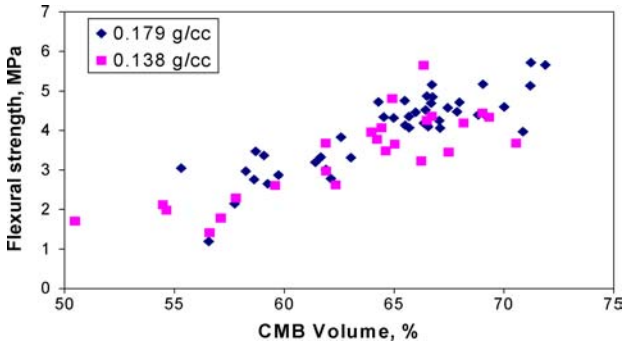

Figure 11 Flexure strength data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

Fig. 11 contains the flexure strength of samples collected on syntactic foam materials made from high and low density CMBs. The data shows an increase in flexure strength with increasing CMB volume percent. Furthermore, though there is some scatter, the two data sets overlap. Plotting this strength as a function of bulk density, see Fig. 12, one would expect to see the data sets to separate by CMB density. This is not the case, though the trend is that the 0.138 g/cm^3 CMBs tended to have somewhat higher flexure strengths at a given density. The explanation for this is not obvious and will be investigated further in future research.

Figs 13 and 14 are the flexural modulus values as a function of CMB volume percent and bulk density, respectively. As in the flexural strength, flexural modulus data show the trend of increasing with increasing CMB volume percent, see Fig. 13, and is not dependent on the CMB tap density (i.e. the data sets overlap). When flexural modulus is plotted against bulk density, the tap density data sets do separate. At a given density the foam made with the lower tap density CMBs have a higher modulus. Taking into consideration Figs 13 and 14, flexure modulus, in this CMB density range, is dependant only on the volume percent of CMBs and not the amount (mass) of carbon present at that volume percent. The physical explanation for this increase is that as the PF increases, the CMBs are closer together and the more CMB-CMB bonding occurs by the APO-BMI, which is the controlling factor in flexural modulus.

4. Conclusions

1. At a constant CMB volume percent, foams made from higher density CMBs produce a foam with higher compressive strength and modulus.

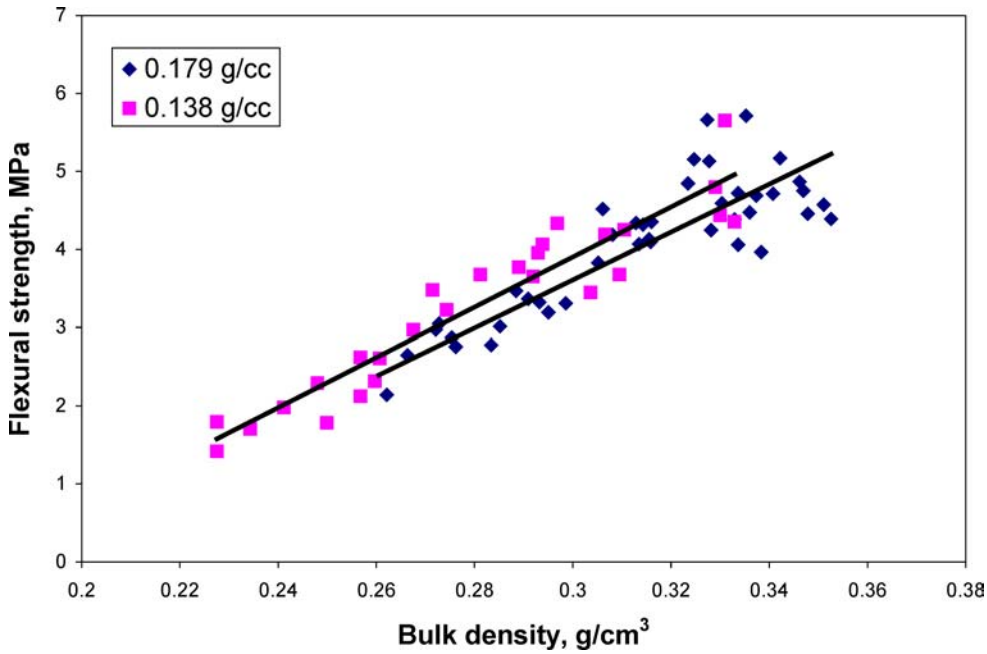

Figure 12 Flexure strength data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

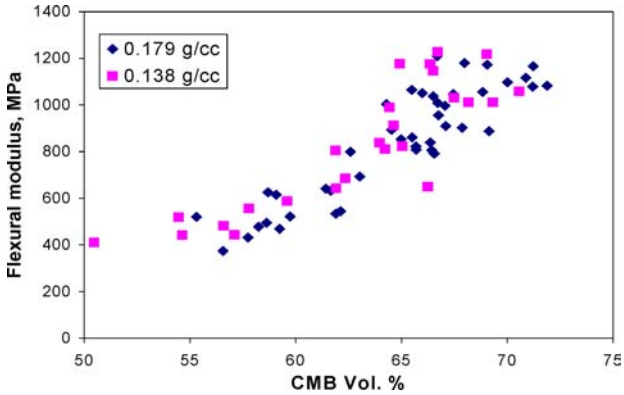

Figure 13 Flexure modulus data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

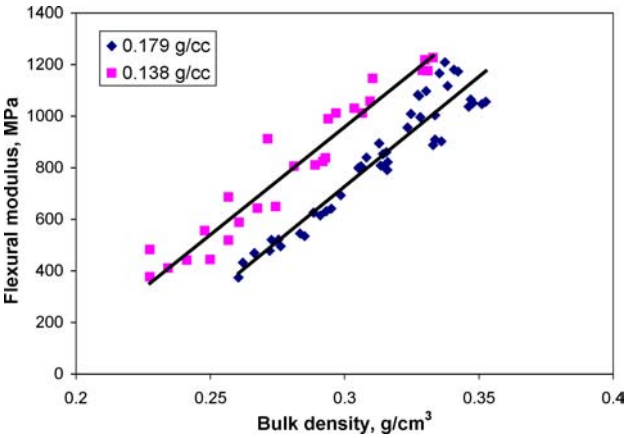

Figure 14 Flexure modulus data comparing syntactic foams made from CMB of ρ_{tap} 0.138 and 0.179 g/cm^3.

2. At a given bulk density, compression strength and modulus depends on volume percent of the CMBs. The explanation can be thought of in terms of the arrangement of carbon or in terms of types of void.

a. The arrangement of mass (carbon) is important in the compressive behavior and design of syntactic foams. At a given foam density (constant MB/binder mass ratio), the compression strength will increase by using lower density CMBs (smaller t/d ratio) at higher volume percents. In other words, to design a stronger foam, it is better to have a high volume percent of thinner-walled MB thus, increasing the number of load paths through the material.

b. Interstitial and contained void are not equivalent. To maximize the compression strength (at a given foam density), the interstitial void should be minimized or exchanged for contained void.

3. At a given MB volume percent, flexural strength and modulus are independent of CMB density. The implication of this, although only definitely seen in the modulus data, is that at a given bulk density, foams made from lower density CMBs have a higher flexural modulus than those made from higher density CMBs because of volume fraction differences.

4. Optimization of both compressive and flexure properties at a given density is accomplished by maximizing the volume percent of the CMB phase. This can be achieved by packing the lowest density CMB possible into the composite without significant breakage occurring. Packing a mono-modal distribution of spherical particle one can achieve a packing factor of 68-70%.

5. To completely describe a three-phase syntactic foam the following must be specified: a) MB density, b) MB volume percent, c) binder volume percent, and d) foam density (although this value can be calculated knowing a, b, and c, in a practice it is needed because breakage of MBs is inevitable).

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