J MATER SCI **41** (2006) 4009–4014

Microstructural failure modes in three-phase glass syntactic foams

M. KOOPMAN, K. K. CHAWLA, K. B. CARLISLE
University of Alabama at Birmingham, 1530 Third Ave. South, BEC 254, Birmingham, AL, 35294-4461, USA

G. M. GLADYSZ
Los Alamos National Laboratory, Los Alamos, NM, 87545, USA

Published online: 7 June 2006

Samples of syntactic foam containing hollow glass microspheres of 0.108 and 0.253 g/cm^3 tap densities, some with a silane surface treatment, were subjected to different stress states and examined for failure modes. All foams contained the same volume fraction of APO-BMI, a bismaleimide resin binder. The samples were tested in compression and in three-point bend, and mechanical properties were compared between the various foams. Microsphere strength had a strong effect on overall uniaxial compressive strength with interface strength playing a secondary, yet significant role. In three-point bending, the role of the interface was much more critical. Cross sections of the compression test samples were examined by optical microscopy, and fracture surfaces were investigated by scanning electron microscopy.

1. Introduction

Two-phase and three-phase syntactic foams are finding increasingly diverse applications, ranging from packaging materials for expensive components to the core material in sandwich structures used in aerospace, transportation and deep sea submersibles. These materials are attractive due to their low density, good specific strength and their acoustic and thermal damping properties. The mechanical properties of syntactic foams and their sandwich structures have been widely studied in compression and in three-point bend, but little has been published concerning the microstructural failure modes of these materials when subjected to specific stress states, particularly of three-phase syntactic foams.

Three-phase syntactic foams, which by definition contain interstitial porosity in addition to hollow microspheres and a binder phase, are somewhat anomalous to conventional approaches to fracture mechanics. [1] For example, the interstitial porosity of three-phase syntactic foams can be regarded as inherent flaws for crack initiation, but the definitions from fracture mechanics of radius of curvature at the crack tip and crack length can not readily accommodate the convoluted morphology of the interstitial porosity. In addition, when one combines the volume of the contained porosity of the microspheres with the interstitial porosity, these materials can have in excess of 90 vol.% porosity. This represents a rather extreme circumstance from the perspective of solid structures.

In the present study, we have examined three syntactic foams, including foams incorporating hollow glass microspheres of two different isostatic crush strengths and two surface treatments, which affected the interface strength between binder and microsphere. We have attempted to determine which components of the foam are failing under certain imposed stress states by examining fracture surfaces from compression samples and from the tensile side of three-point bend samples. By combining this information with macroscopic measures of foam strength in uniaxial compression and three-point bending, we have sought to gain insight into the microstuctural failure modes in these three-phase syntactic foams.

2. Materials and experimental procedure

Two types of glass microspheres were obtained from 3M Co., A16 and B38 and were used to produce syntactic

[1] "Microspheres' will hereafter refer to "hollow microspheres".

0022-2461
DOI: 10.1007/s10853-006-7601-9

TABLE I Properties of glass microspheres

Tap densiy (g/cm^3)	3 M product code	Isostatic crush pressure (MPa)	True density (g/cm^3)
0.108	A16/500	3.4	0.16
0.253	B38/4000	27.6	0.38

foams for this investigation. Details of the two types of hollow microspheres are given in Table I. At the rated isostatic crush pressure, 3M Co. targets 90% survival of hollow microspheres with a minimum survival rate of 80%. Two types of foam were made from the A16 microspheres, the first incorporating "as received" microspheres and the second with a 2% Silane coating. The B38 microspheres had a coating of silica particulate for anti-caking, which served to create a particularly weak microsphere/binder interface. All three foams used 8.5 vol.% APO-BMI, a bismaleimide resin, as a binder and were processed under identical proprietary conditions at Los Alamos National Laboratory. Five samples were run for each of the foams in compression and six samples for each of the foams in three-point bending.

Compression and three-point bend tests were done on an Instron 5500 R mechanical test frame equipped with a 2 kN load cell. Samples for compression testing were cylindrical with an approximate diameter of 28.7 mm and height of 25 mm. Compression tests were run at 2% strain/min and were terminated at some point after ultimate compressive strength was reached. Samples for three-point bend tests had dimensions of approximately $76.2 \times 10.1 \times 4.0$ mm, and with a support span of 49.1 mm.

Scanning electron microscopy of Au-Pd sputter coated samples was performed with a Philips 515 SEM in secondary electron mode. Optical images were taken on a Zeiss Axioplan 4 MP after cross sectioned metallographic preparation.

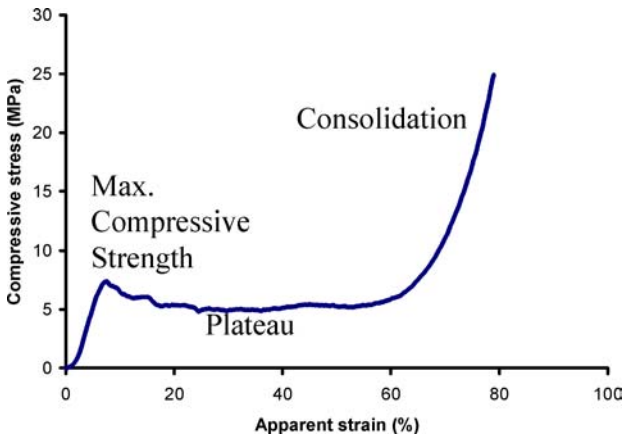


Figure 1 Stress-apparent strain curve for a B38 glass microsphere syntactic foam showing an initial linear elastic loading segment, ultimate compressive strength, plateau region and final consolidation of the failed foam.

3. Results and discussion

A typical compression stress-strain curve of a syntactic foam, Fig. 1, showed an initial linear elastic loading segment and a subsequent maximum compressive strength, followed by a plateau region and finally a steep increase where compaction and consolidation of foam material

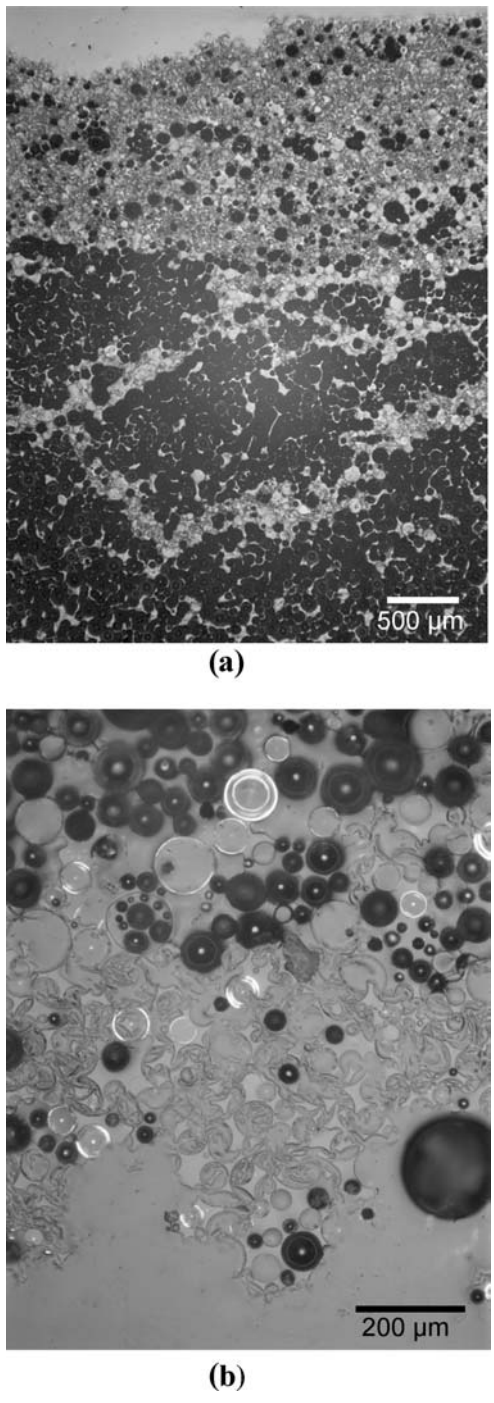


Figure 2 Optical micrographs showing: (a) large band of foam failed in compression near the upper platen with smaller bands propagating into the interior of the sample and (b) a higher magnification image showing the survival of particular microspheres within the failed band, particularly the largest and smallest microspheres.

occurred. The maximum compressive strength represents the point at which fracture initiates, and the plateau region represents the constant stress at which microspheres within the foam fail [1–3]. Several authors have noted that when the weakest microspheres fail, their loads are transferred to neighboring microspheres and binder or matrix, thus propagating the compressive failure [1, 2]. In the present work, bands of failed material were noted, Fig. 2, but rather than failure in the center of the sample, as noted by Kim *et al*. [2], the primary bands were observed near the platen surfaces, possibly due to shearing effects and friction with the platens. The bands seen in Fig. 2, which propagated diagonally toward the center of the sample, followed similar types of paths to those noted by Gupta *et al*. [1], which were attributed to shearing forces in rectangular compression samples of varying aspect ratios. Rizzi *et al*. [4] have suggested that such bands encourage sliding of the two surfaces against one another with corresponding friction and interlocking of the opposing sides, thus possibly accounting in part for the residual strength of the plateau region. Such effects cause strain localizations. Of particular note in the higher magnification image of Fig. 2b is the retention of intact microspheres within highly consolidated bands. Work on the compressive strength of individual microspheres by the authors indicates that larger diameter glass microspheres tend to fail at higher loads [5]. Fig. 2b shows a range of sizes of surviving microspheres within failed bands, but with a prevalence of larger microspheres, which can withstand higher loads, and smaller microspheres, which may rest in pockets surrounded by sections of foam that are still carrying load.

The variation of the maximum compressive strengths of the three foams as a function of the tap density of their microspheres is shown in Fig. 3. The foam comprised of B38 microspheres with a 0.253 g/cm^3 tap density showed the highest compressive strength, corresponding to the relatively superior isostatic crush strength of those microspheres. The two foams consisting of A16 microspheres, however, showed a clear distinction between the two populations with no overlap in standard deviation between the coated and uncoated microspheres. Thus, although the primary determinant of compressive strength may be the compressive strength of the constituent microspheres, the interface characteristics of the system can play a role in compressive properties. Although a Silane coating might be expected to increase the bond strength between glass and the polymeric binder phase, in this case the interaction between the Silane and a methacrylato chromic chloride coating applied to this grade of microsphere by 3M Co. produced a weaker interface than the "as received" microspheres with only the methacrylato chromic chloride treatment.

The B38 microspheres, which were coated with particulate silica, as an anti-caking agent, significantly weakened the interface between the binder and microspheres. This demonstrates the predominance of microsphere strength in relation to other microstructural effects which contribute to the overall compressive strength of foam, since this foam had in excess of three times the compressive strength of the foams comprised of A16 microspheres. SEM images of the B38 microspheres before and after ultrasonic cleaning in methanol are shown in Fig. 4, (note the clean smooth surface after removal of the anti-caking agent). Several of the foams with B38 microspheres also demonstrated vertical splitting in compression as a result of their weakened interfacial character. An example of a fracture surface from a vertical split is shown in

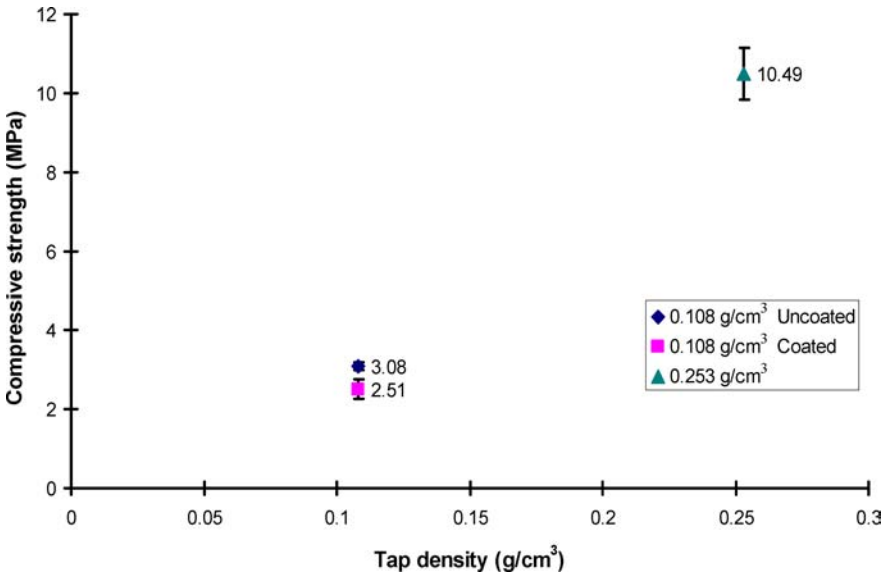
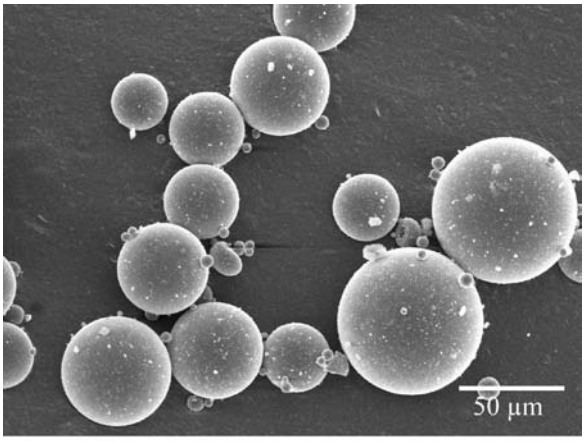
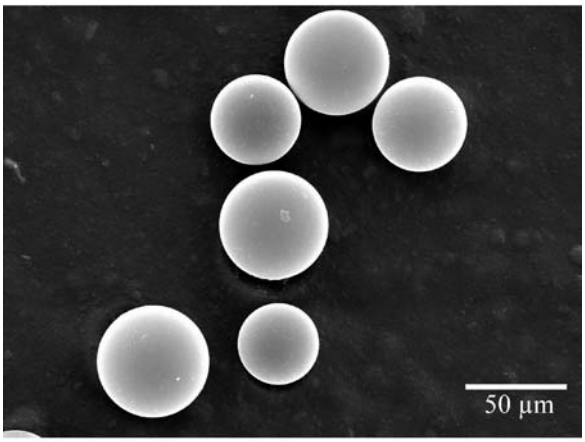


Figure 3 Average maximum compressive loads with standard deviations, show a much higher compressive strength for the foam with 0.253 g/cm^3 tap density glass microspheres, but also a distinct difference between the coated and uncoated foams of lower tap density microspheres.



(a)



(b)

Figure 4 Images of B38, 0.253 g/cm^3 microspheres; (a) "as received", and (b) after ultrasonic cleaning in methanol, showing the presence, and absence, respectively, of a silica anti-caking agent.

Fig. 5, and higher magnification images of the fracture surface are shown in Fig. 6. In Fig. 6 one can observe smooth surfaces of intact microspheres, as well as areas of binder phase with smooth spherical arcs where the interfaces have failed. These views of intact microspheres in a syntactic foam are rather rare, since in fractured foams, sectioned or sawn foams or even in "as formed" materials, the nature of the material tends to exhibit broken microspheres at the surface. Palumbo *et al*. [7] noted a similar feature in a two-phase thermally cured syntactic foam of glass microspheres. In their work, the thermally cured samples also showed cracking at the matrix/microsphere interface, and these results were compared to the same system having been cured in a microwave field where the interface was somewhat stronger. In fact, an observation of predominantly unbroken microspheres in a foam indicates that the materials were either inadequately mixed or that weak interfacial characteristics were present in the system.

The results of three-point bending tests, given in Fig. 7, show the highest values from the foams with uncoated

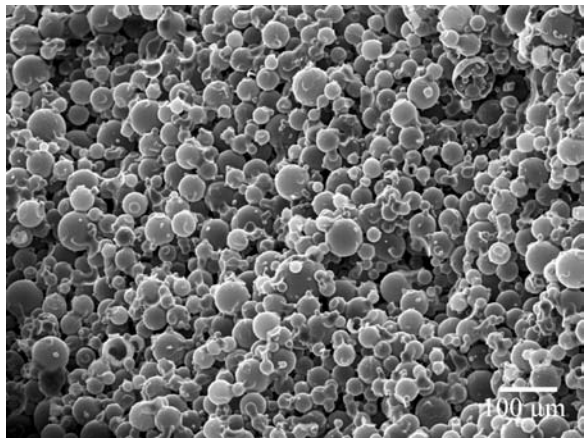
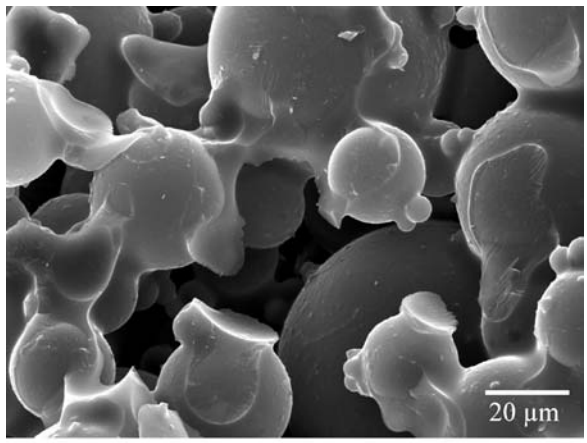
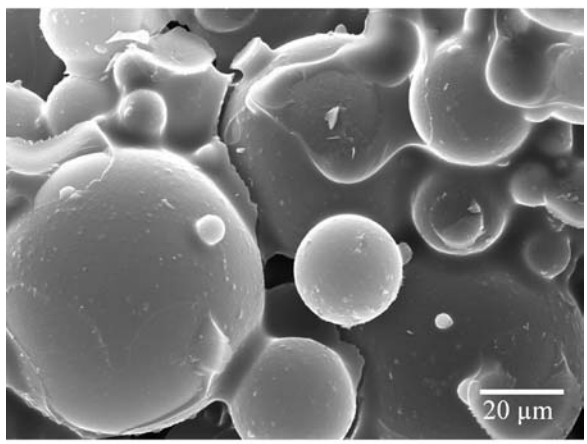


Figure 5 Image of the fracture surface from a vertical split in a foam containing B38 microspheres. Note the absence of broken microspheres and, therefore, the predominance of interface failure.



(a)



(b)

Figure 6 Higher magnification images of the fracture surface shown in Fig. 5; (a) binder/microsphere interface failure, and (b) a crack propagating along interfaces between binder and microspheres.

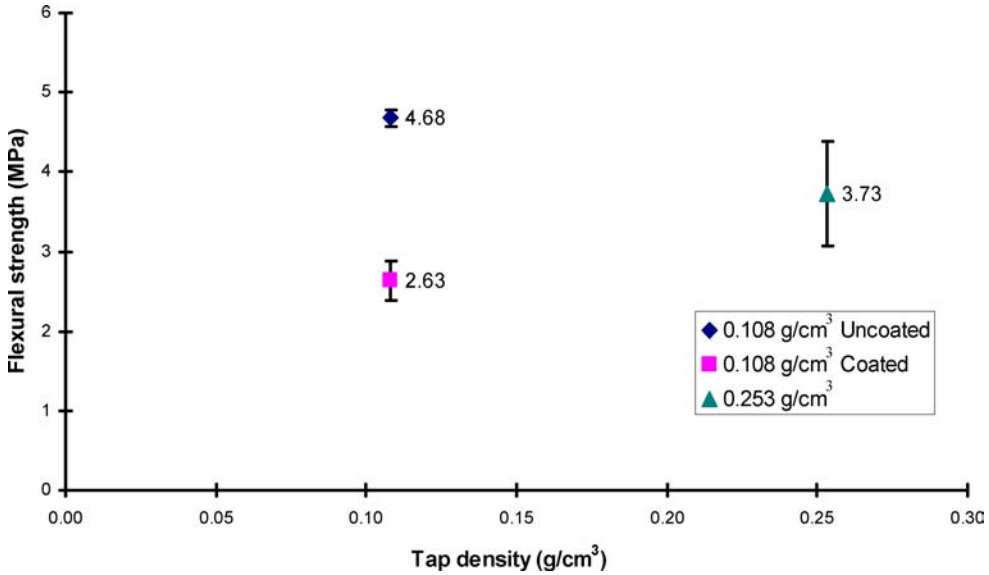


Figure 7 Three-point bend strength, showing average and standard deviations for the three foams as a function of tap density.

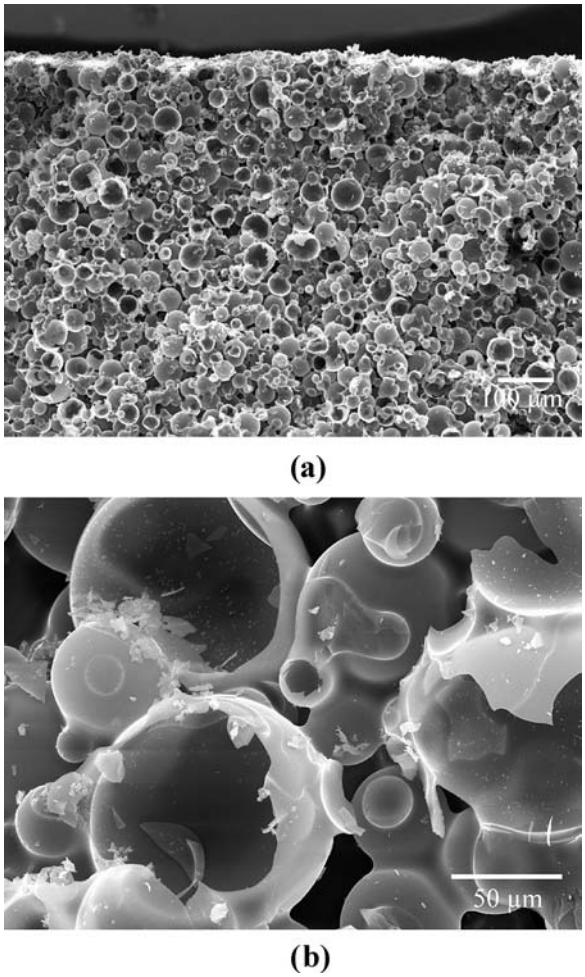


Figure 8 Fracture surfaces from the tensile side of a foam containing uncoated A16 microspheres tested in 3-point bend; (a) lower magnification and, (b) higher magnification, showing broken microspheres.

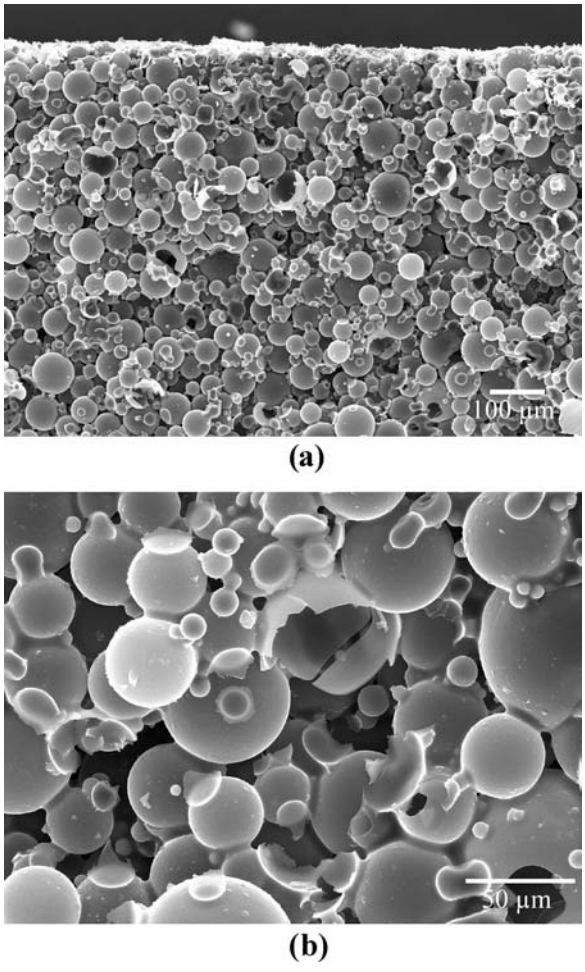


Figure 9 Fracture surfaces from the tensile side of a foam containing uncoated B38 microspheres tested in 3-point bend; (a) lower magnification and, (b) higher magnification, showing some broken microspheres, but significantly more interfacial failure than the foam containing A16 microspheres.

A16 microspheres. Examples of fracture surfaces from the tensile side of three-point bend tests on foams containing uncoated A16 and "as received" B38 microshperes are shown in Figs 8 and 9, respectively. A much lower incidence of observable interface failure occurred in the foams containing A16 microspheres, Fig. 8. This, combined with the higher disparity in three-point bend strength between foams containing coated and uncoated A16 microspheres, compared to the difference between the values of these foams in compression, suggests that the role of interface strength may be much more important to three-point bend strength than it is to compressive strength. The relative importance of the interface in three-point bending is further validated by the lower three-point bend strength of the foam containing B38 microspheres with correspondingly weak binder/microsphere interface strength compared to the foam with uncoated A16 microspheres, despite the B38 having a much higher crush strength. The strong effect of interfacial debonding, as well as binder failure, in three-point bend tests was noted by Karthikeyan *et al*. [8] in the study of two-phase glass microsphere syntactic foams with and without chopped fiber reinforcements. Although the load transfer would be different when comparing two-phase and three-phase foams, one would anticipate a relatively greater dependence of interfacial strength on overall three-point bend strength in a three-phase foam, since there is less binder, or matrix, to bear the load in three-phase foams.

The relative mechanical properties of the binder phase, the microspheres and the interface, combined with morphology and imposed stress state, create a complicated scenario, but one in which latitude of design for specific applications exists. Microsphere composition, average size, size distribution, morphology and wall thickness can be selected, as well as type and vol.% of binder phase. In addition, coatings which strengthen or weaken the interface may be applied to the microspheres before production of the syntactic foams. Several of these factors have been shown, in the current work and in the literature, to change the foams reaction to specific stress states.

4. Conclusions

In the present work, microsphere strength had a strong effect on overall uniaxial compressive strength with interface strength playing a secondary, yet significant role. In three-point bending, the role of the interface was much more critical. As other researchers have noted, various coatings have a profound effect on interface strength and in the system studied here, the microsturctural effects of these coatings were directly observed after failure in uniaxial compression and on the tensile side of three-point bending by SEM and compared to overall foam properties. Primarily interface failure was observed and characterized as the presence of intact microspheres with clean surfaces, accompanied by corresponding areas of binder with concave spherical sections. The presence of surviving intact microspheres within highly consolidated bands in compression samples was also noted. Further investigation of such microspheres might aid in the understanding of relative properties of microspheres within a given population.

Acknowledgments

This work was supported by Los Alamos National Laboratory/U.S. Department of Energy, Grant # 44277-001-02 4X.

References

1. N. GUPTA, E. WOLDESENBET and P. MENSAH, *Composites Part A: Applied Science and Manufacturing* **35**(1) (2004) 103.
2. H. S. KIM and P. PLUBRAI, *Composites Part A: Applied Science and Manufacturing* **35**(9) (2004) 1009.
3. N. GUPTA, KISHORE, E. WOLDESENBET and S. SANKARAN, *J. Mater. Sci.* **36**(18) (2001) 4485.
4. E. RIZZI, E. PAPA and A. CORIGLIANO, *Int. J. Solids and Structures* **37**(40) (2000) 5773.
5. M. KOOPMAN, G. GOUADEC, K. CARLISLE, K. K. CHAWLA and G. GLADYSZ, *Scripta Materialia* **50** (2004) 593.
6. N. GUPTA, E. WOLDESENBET and KISHORE, *J. Mater. Sci.* **37**(15) (2002) 3199.
7. M. PALUMBO and E. TEMPESTI, *Acta Polym.* **49** (1998) 482.
8. C. S. KARTHIKEYAN, S. SANKARAN and KISHORE, *Polym Int.* **49** (2000) 158.