Processing and Compressive Strengths of Syntactic Foams with and without Fibrous Reinforcements

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ABSTRACT: Syntactic foam composites containing 0, 0.9, 1.76, 2.54, 3.54, and 4.5 vol % of E-glass fibers in the form of chopped strands were fabricated and subjected to compression testing. It was found that the compressive strength values generally increased with fiber content except for the 3.54% fiber-bearing cast slab, which recorded lower values. This lone exception was due to the difference in processing route adopted in fabricating this particular fiber-bearing foam. Also noticed was the fact that the compressive strength of the 0.9 vol % fiber-bearing system was lower compared to the fiber-free system. This was correlated to the higher level of void content noticed with this fiber-bearing foam compared to that seen in the unreinforced foam. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 405–411, 2001

Key words: syntactic foams; microballoons; glass fibers; compressive strength

INTRODUCTION

Syntactic foams (SFs) are composite foam materials, which are derived by embedding hollow microspheres (microballoons) in a polymer matrix designated as a binder. Because they are similar to cellular, gas blown (chemically or mechanically) plastics, they are grouped along with the foamed plastics.[1] The point of difference lies in the number of phases constituting the system: SFs are a tertiary phase system[2–4] whereas conventional foams are binary.

Syntactic foams are also categorized as physical foams[5] because the matrix is not foamed chemically but the gas containing particles are filled mechanically into the matrix. Because the sizes of the gas containing particles can be tailored to within a close range, foams of higher order or regularity are obtainable and hence termed syntactic. These materials can also be viewed as reinforced polymers because glass and ceramic microballoons can be considered as reinforcing the polymer matrix material. Compared to conventional foams, SFs are truly closed-cell foams, having better strength to weight ratios and negligible water absorption properties. Further, these foams are heavier than the conventional foams with apparent densities of 200–800 kg/m^3. Inclusion of hollow microspheres into the system yields a material that is much lighter than that obtainable with conventional fillers such as glass powder, talc, kaolin, and so forth. Due to the rigidity of the glass microballoons, they are mechanically superior to the other cellular gas blown foams. In brief, SFs have great potential for use as high performance composites for structural applications, apart from the well-known microwave transparency applications.

Microballoons can be made of glass, phenolic, carbon, ceramic, metallic, and polymer based ma-

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terials. The binders used are normally thermosetting resins such as epoxy,[6] polyester,[7] phenolic,[8] etcetera. Of these, the epoxy SFs are popular because they can be tailored to suit the requirements in the end product. Although the high viscosities of epoxies are a disadvantage, the problem can be tackled by resorting to suitable processing techniques and/or selection of the material. Bisphenolic, novolac, and the other structured epoxy resins in combination with glass phenolic microballoons have been used to make SFs.[6] Also, reports in the literature concerning epoxy SFs incorporating polystyrene,[9] carbon,[10] and mineral[11] microballoons can be found.

These SFs as a core material also found application in the construction of sandwich structures.[12,13] Because the processing is mechanical, entrapment of some amount of air leading to the formation of voids is inevitable. Therefore, on the basis of their structures, SFs are classified as either two- or a three-phase foams.[14] Among the newer composite systems, SFs have caught the attention of structural engineers and material scientists because these have low densities and are useful as buoyancy-aid materials.[15,16] In these subsea applications, a property of considerable importance is the behavior in compression. The other significant property generally looked for is the moisture absorption and the attendant property degradation. Because these foams are made from closed pore material, the latter aspect of water absorption would be less critical when viewed from the angle of microballoons, which is a major constituent of the SF.

Because the mechanical properties of the SFs are dependent upon the density of the foam, which in turn is dependent upon the resin/microballoon ratio, an earlier study[17] showed that as the density increases the strength rises. In the present report the first aspect, namely, the compression behavior of SFs, is considered. Here, unlike reinforcement with fibers of the continuous fabric-form type reported in the literature,[18] fibers in the form of chopped strands were chosen for incorporation and the behavior of the resultant material was compared with fiber-free systems. Further, the report addresses the issue of the introduction of epoxy compatible glass fibers of varying levels and the attendant changes that occur in regard to the compressive strength. This approach was adopted because hitherto no attempt of this nature could be cited based on a survey of the available literature. Also, the scope of the work was expanded to include the fabrication of foams of density higher than the usual levels in order to achieve higher strength and thereafter conduct a detailed microscopic examination on the post compression tested samples so that a structure–property correlation could be attempted.

EXPERIMENTAL

Materials

A room temperature curing epoxy resin system consisting of Araldite LY5052 (epoxy novolac system containing 1,4-butanediol diglycidyl ether) and HY5052 hardener (cycloaliphatic polyamine) supplied by Hindustan Ciba-Geigy Ltd. was used in fabricating the SFs. The resin and hardener were mixed in a ratio of 100:38 by weight. The density of the cured resin system was 1.15 g/cm^3. Glass hollow microspheres (microballoons, Ecospheres SI, supplied by Grace Electronic Materials) with diameters in the range of 10–100 μm and a density of 0.25 g/cm^3 were used as closed pore materials. Epoxy resin compatible E-glass fibers in the form of chopped 6-mm length strands (FGP India Ltd.) were used for incorporation into the SF system.

Processing

Table I gives the details about the densities of the fabricated foams and the volume percentages of the resin system, microballoons, glass fibers, and voids in each cast slab. Also given in Table I are the identification codes allotted for the fabricated foams. Reinforced SFs (RSFs) E1SF–E5SF correspond to five RSFs containing, respectively, 5, 10, 15, 20, and 25% by weight of epoxy compatible glass fibers with respect to the resin. The corresponding volume percentages of fibers in the composite system for E1SF–E5SF are 0.9, 1.76, 2.72, 3.51, and 4.51, respectively. From the perusal of Table I, it is evident that, although the volume percentage of fibers varies from E1SF to E5SF, those of the volume matrix and microballoon are almost kept constant. It is also clear that the void volume percentages in the reinforced foams are comparable.

The procedure adopted for fabricating RSFs involved introduction of glass fibers into a beaker that contained the required quantity of resin. The mixture was stirred well for the uniform dispersion of the chopped fibers. A stoichiometric quan-

Table I Volume Percentages of Constituents in Fabricated Syntactic Foams

Slabs	Density (kg/m^3)	Volume Percentage			
		Matrix	Microballoon	Fibers	Voids
SF	670	46.96	52.58	—	0.45
E1SF	621	41.84	47.62	0.9	9.61
E2SF	633	40.83	46.64	1.76	10.74
E3SF	671	41.94	47.80	2.72	7.55
E4SF	676	40.56	46.51	3.51	9.39
E5SF	720	41.82	47.58	4.51	5.96

tity of hardener was mixed in and stirred well. At this stage a weighed quantity of microballoons in several lots was added at regular intervals to the system containing the resin mix and fibers, stirring the contents well each time. Mixing was done as gently as possible in order to avoid breakage of the microballoons till such time that the mix developed a dough form. The dough was later transferred into a metallic mold measuring 150 × 150 × 25 mm. The mold was then closed and allowed to first cure for 18–24 h at ambient temperature and later postcured for 2.5 h at 130°C. This procedure was consistently followed for the fabrication of four (i.e., E1SF, E2SF, E3SF, and E5SF) of the five categories of foam slabs.

For making the fifth slab (E4SF), however, a variation in the procedure as detailed below was followed. In this case, too, the stoichiometric quantities of resin and hardener were placed in a beaker and stirred mechanically. The weighed quantity of microballoons was added in several lots to the resin system, and the contents were well stirred each time. To this the glass fibers were added and mixed well to get a dough form. In the former case involving the making of the four slabs (i.e., E1SF, E2SF, E3SF, and E5SF) the fibers were added initially while in the latter (i.e., E4SF) case the fibers were introduced at the end. Thus, a procedural change during the fabrication stage was effected in order to study how this variation in processing methodology would affect the response the material had during compression loading. The curing procedure of this E4SF slab made by introducing fibers at a later stage of mixing the constituents was identical to the one adopted in making the other four fiber-bearing systems detailed earlier.

From the perusal of Table I it is evident that the (unreinforced) SF had an insignificant quantity of voids; hence, it may be viewed as a two-phase foam for discussion purposes. The reinforced foams, on the other hand, had significant amounts of voids varying from 6 to 10%. The presence of such voids could have a bearing on the mechanical properties. Simultaneously, their presence in the foam slabs had the effect of reducing the density of the material.

Compression Testing

The test specimens with 15 × 15 × 7.5 mm dimensions conforming to ASTM D 1621-73 were sectioned from the fabricated foams. The compression testing was done in a servohydraulic microprocessor controlled DARTEC 9500 machine operated at room temperature and a true strain rate of 0.01 s^{-1}. The testing was programmed to terminate on reaching 50% of the initial height of the specimen. The compressive strength was calculated from the data output. The average values derived from tests on a minimum number of five specimens are depicted in Table II.

Scanning Electron Microscopy

The compression test subjected samples were coated with a conducting layer using a sputtering

Table II Compression Test Data of Fiber-Free and Fiber-Bearing Syntactic Foams

Sample	Compressive Strength (MPa)	Specific Strength (MPa/kg/m^3)
SF	57.51	0.0858
E1SF	51.36	0.0828
E2SF	61.00	0.0929
E3SF	67.61	0.1009
E4SF	52.36	0.0774
E5SF	76.42	0.1061

unit and were examined in a Jeol JSM-840A scanning electron microscope (SEM). Typical surface features were recorded.

RESULTS AND DISCUSSION

Table II shows the compressive strength data for fiber-free and fiber-bearing SFs. It is evident that the compressive strength values generally showed an increase as the volume percentage of fibers increased, except for the E4SF slab, which followed a different fabrication procedural route as mentioned earlier. This general pattern of an increase in strength can be attributed to the increased load-bearing capacity of the fibrous reinforcements, despite their levels of voids between 6 and 11% (Table I). Thus, the results indicated that introduction of fibers assisted in altering the response of the material during compressive loading.

The processing route adopted for the E4SF foam (the introduction of fibers at the end) led to a situation where a greater number of regions displaying accumulated voids resulted. This account was substantiated by the findings of the non destructive evaluation technique reported earlier.[19] Because of these voids the strength comes down. Another consequence accruing out of the process modification was the nonuniform distribution of fibers in the E4SF system result compared to the other four foam slabs. This difference in distribution was because of the fact that the fibers were unable to spread themselves in a medium in which instead of only the resin being present, a resin containing glass microballoons was well mixed into it. Each of these glass spheres could act as an obstacle for any tangible distribution of fibers, which possess a definite aspect ratio. The net effect of all such situations should be the bunching of fibers. This was shown in the section dealing with scanning electron microscopy to be detailed later. Due to this bunching, the spread of the resinous material on the surface of the fibers would be restricted. The transfer of the load from the matrix to the individual fibers was therefore less evenly and effectively achieved. This was also reflected in the recording of a different compressive strength value for the E4SF slabs.

As mentioned earlier, E1SF, E2SF, E3SF, and E5SF foams were processed by following a common procedure. Hence, the results of these varieties can be compared. When the density increased from 621 to 720 kg/m^3, the compressive strength registered a raise from 51.4 to 76.4 MPa for E1SF–E5SF, respectively (Table II). The data further pointed to the fact that when keeping the volume percentages of the matrix and microballoons nearly the same and for a comparable level of void content (Table I) in the reinforced foams, the compressive strength increased with the volume percentage of the fibers. In other words, the achievement of the twin effects of increasing the density and fiber content of the slab system (Table I) resulted in the recording of increased strength values in compression (Table II).

Comparing the compressive strength values of fiber-bearing (E1SF) and fiber-free foams (SF), the latter showed a higher value than the former (Table II). This was attributed to the low volume percentage of voids ($<$0.5%) and higher density (670 kg/m^3) in fiber-free foam (SF) compared to 9.6% voids and 620 kg/m^3 density exhibited by E1SF (Table I). With regard to E2SF, although it had a higher void content (10.74%, Table I), it, unlike E1SF, still showed higher compressive strength compared to the fiber-free one (SF, Table II). The principal cause for this difference in performance for E2SF could be traced to the enhanced presence of fibers and their participation during loading. Comparing the similarly processed E3SF and E5SF foams possessing similar density levels showed that the latter with a larger fiber content displayed higher strength, emphasizing again the role played by fibers in strengthening the foam material. An outcome of the investigation was the fact that if voids can be reduced in the material, a still higher level of mechanical properties is achievable in the material. To better understand this mechanical behavior the microstructural details were examined with a SEM. The salient observations recorded are listed below.

SEM Studies

Figure 1 is the SEM picture of the compression tested fiber-free (SF) sample. As is evident from the photograph, a sizeable proportion of the microballoons was not damaged, despite subjecting them to compressive deformation. Instead, a slight debonding of microballoons from the matrix was seen. Figure 2 illustrates the features in the compression tested E1SF sample. In this case the features revealed a sizeable quantity of microballoons being appreciably damaged and further the resulting debris spread around. Thus, there was a distinct difference in the deformation scenario between reinforced and unreinforced samples. This

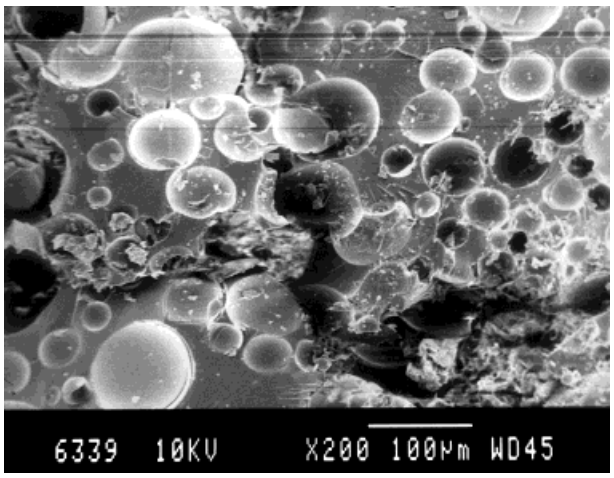

Figure 1 An SEM picture of the compression tested fiber-free syntactic foam sample.

observation, therefore, lent a new contribution from the structural side, which can account for the decreased strength values. Earlier on, the concept of the level of void content was invoked to explain the lowering of strength in E1SF compared to SF. In this way the utility of microscopic examination in correlating the mechanical properties was clearly brought out in this investigation.

Additional details regarding the differences in the responses of the RSFs were sought in this work through this microscopy approach. Some of the observations recorded are now presented and their significance highlighted. Thus, Figure 3 shows the micrograph of the compression tested E2SF sample. It is evident that, as in the E1SF case, the distribution of debris around the microballoons was seen.

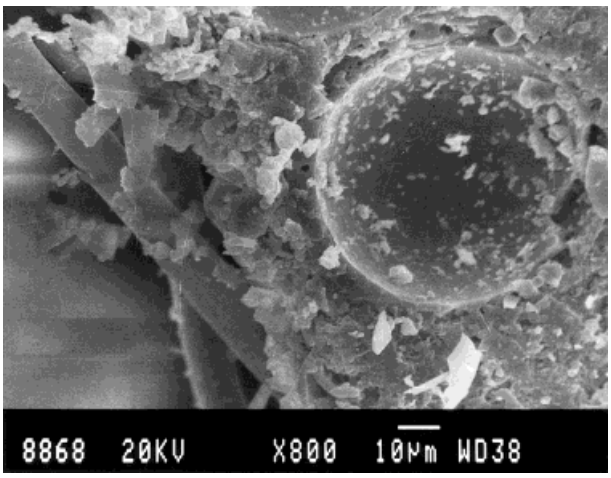

Figure 3 An SEM picture of the failed E2SF sample.

Although the matrix showed features of deformation markings, the fibers and microballoons still effectively participated in sustaining the applied load, thereby making this larger level reinforced variety (i.e., E2SF) yield better strength than the fiber-free system. Figure 4 shows the compression failed E3SF foam sample; regions containing the interfaces of the microballoon–matrix and fiber–matrix (indicated by two marked arrows emanating from a common origin) are noticeable. The features in the compression tested E5SF sample are shown in Figure 5. Matrix deformation, fiber protuberance, and microballoon damage in one case and debonding in the other are evident from this SEM picture (Fig. 5).

Coming to the differently processed E4SF variety, Figure 6 shows the SEM feature in a sample

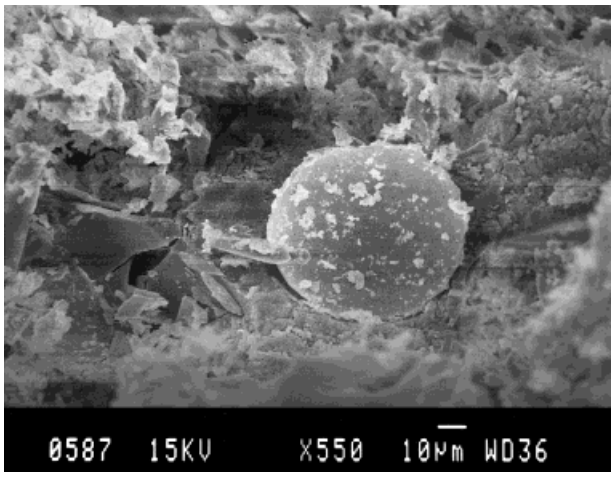

Figure 2 The SEM features in the compression tested E1SF sample.

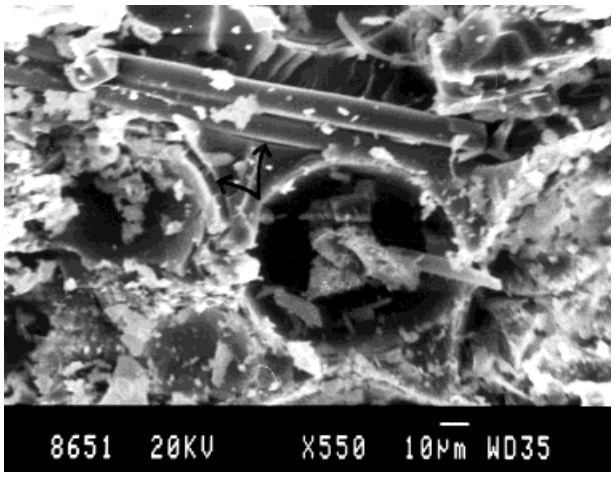

Figure 4 The SEM features in the compression failed E3SF sample.

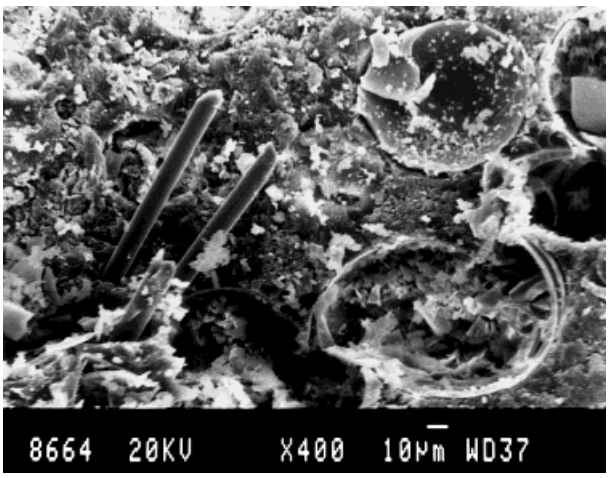

Figure 5 An SEM picture of the compression tested E5SF sample.

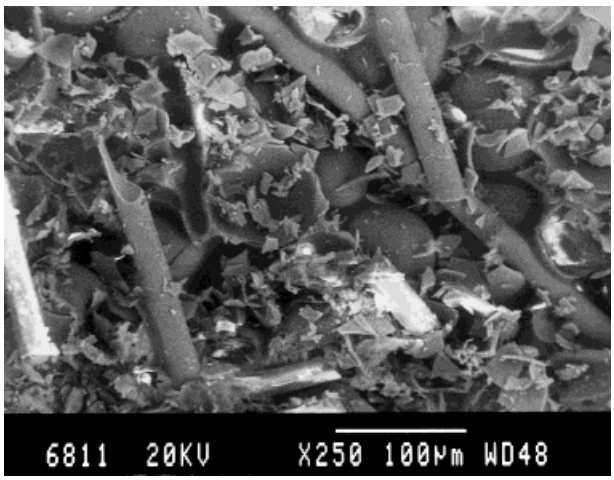

Figure 7 The fracture features in the failed E4SF sample.

prior to compression tests. The bunching together of fibers is distinctly brought out in the Figure 6 scanning micrograph. This bunching caused the wetting of fibers by the matrix (as stated earlier) to be affected. Consequently, discontinuity in the form of voids existed, significantly affecting the transfer of load from the matrix to the fiber. This resulted in a lowering of the compressive strengths. In regard to the compression tested E4SF sample, Figure 7 records such features as the matrix deformation, debris formation, and presence of fibers. Another feature describing the fiber debonding besides deformation in the matrix-rich region around a void is seen in Figure 8. This fiber debonding process could have its origin in the earlier stated incomplete wetting problem associated with this differently processed slab. This second time recording of the microstructure, which had a bearing on the response to the compressive loading, pointed to a new dimension that the structure–property correlation studies can offer in the understanding of the deformation behavior in the compression of these RSF systems.

A cursory glance of Table I gives the density values from which it is obvious that E1SF and E2SF were less dense than the SF, but the specific strength (Table II) for the E2SF foam was higher than the fiber-free SF. Comparing the specific strengths for foams of similar density levels, for instance, SF and E3SF foams (Table II), the latter shows higher values than the former. This observation stresses the utility of introducing fibers into the SF systems.

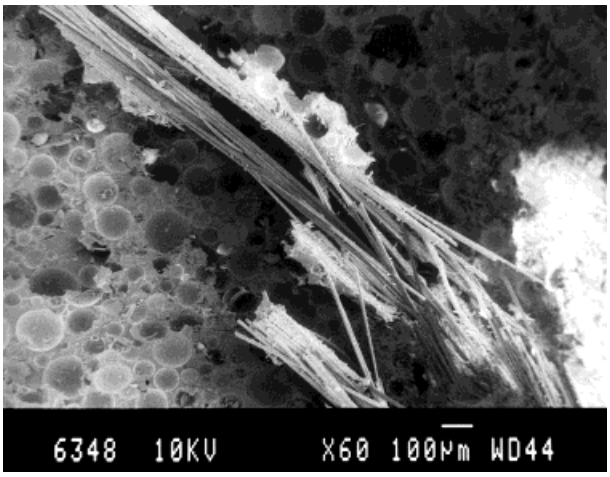

Figure 6 The clustering of fibers in the E4SF sample.

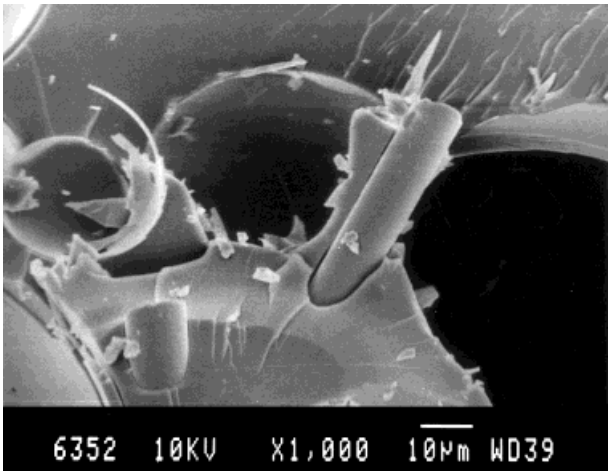

Figure 8 The fiber debonding in the compression tested E4SF sample.

CONCLUSIONS

From the foregoing observation it is clear that, besides noticeable physical features like voids, microstructural variations do have a significant influence on the compressive behavior. Also, the incorporation of chopped fibers into the SF system, initially in smaller proportions, does not help in the improvement of strength of this system. However, at slightly higher levels the fibers aid in strengthening the composite system and add significantly to the specific strength.

Syntactic foams are therefore expected to do better with the incorporation of fibers without much of a change in the density for such end applications as subsea buoyancy-aid materials, where high compressive strengths and low density are considered vital.

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