Mechanical Properties of Polybenzoxazine Syntactic Foams

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ABSTRACT: Syntactic foams of polybenzoxazine, containing moderately high volume percentage of glass microballoons, were prepared. The specific gravity decreased with increase in microballoon content. The disproportionate decrease in specific gravity was ascribed to entrapment of air voids during compaction. The high content of microballoon increased the possibility for air voids that tended to get accumulated. The effect of microballoon concentration on tensile, compressive, and flexural strengths of the foams was studied. Tensile and compressive properties were optimized at about 68% by volume of microballoon while flexural strength decreased marginally on increasing the microballoon content. Althought the specific tensile and compressive strength showed a maximum followed by a decrease, the specific flexural strength systematically increased with microballoon content. The increased packing density of syntactic foam of a given constituent composition increased the compressive strength. The property variation was corroborated by morphological features, as evidenced in scanning electron micrographs. The syntactic foams showed ''multiple resin-neck formation'' and ''disc-shaped microballoon regions.'' The crushing of microballoons during molding was inevitable when compaction was effected to achieve a density beyond the theoretical one. Low-density syntactic foams tend to fail at lower loads because of fracturing of microballoons. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1021–1028, 2008

Key words: polybenzoxazine; syntactic foams; composites; mechanical properties

INTRODUCTION

Polybenzoxazine is a class of thermosetting polymer that belongs to the family of phenolic resins possessing many interesting properties such as high thermal stability, easy processability, good electrical properties and flame retardance, improved toughness, low water absorption, near zero shrinkage upon curing, and good mechanical integrity.[1–5] They are derived via thermal ring-opening polymerization of the aromatic oxazines.[6] Composites of polybenzoxazine with a variety of reinforcing/filler system including nano particulates have been reported.[7–10] Short fiber composites have been processed by us.[11] However, there are no reports on syntactic foams based on polybenzoxazine. The good features of polybenzoxazine matrix render it a good candidate for syntactic foam composites.

Syntactic foams are lightweight materials made of hollow microspheres dispersed in a resin and can be used for structural application.[12,13] Syntactic foams find application in many areas including naval, aeronautical, aerospace, civil, and automotive. Epoxy, polyurethanes, silicones, phenolic resins, etc. are the commonly used resins.[14] Many interesting studies have been reported on syntactic foams, and this material has gained considerable attention in the field of composites.[15–17] They exhibit high compressive response, derived from the resistance of microspheres to compressive loads. When microballoons are used as fillers, specific stiffness will be increased, and so these are preferred in lightweight-structural applications. The mechanical properties of syntactic foams are dependent on the density of the foam, which in turn is dependent upon the nature of microballoon and the resin/microballoon composition.[18,19] The effect of bulk density on the compressive properties of syntactic foams has been investigated.[18,20] Phenolic-based syntactic foams could find applications in thermostructural areas.[21,22]

Higher density syntactic foams show higher strength compared to lower density foams. However, for certain specific application, low-density, moderate strength material is preferred over high-density, high strength materials. In addition, the energy absorption is higher for low-density syntactic foams than for high-density foams. There is still a big challenge in developing lightweight polymer syntactic foams for several applications. This work is an attempt to prepare and characterize polybenzoxazine syntactic foams. The work is intended to prepare lightweight, moderate strength syntactic foams of polybenzoxazine. Hence, the work focuses on foams with moderately high microballoon concentration. The matrix

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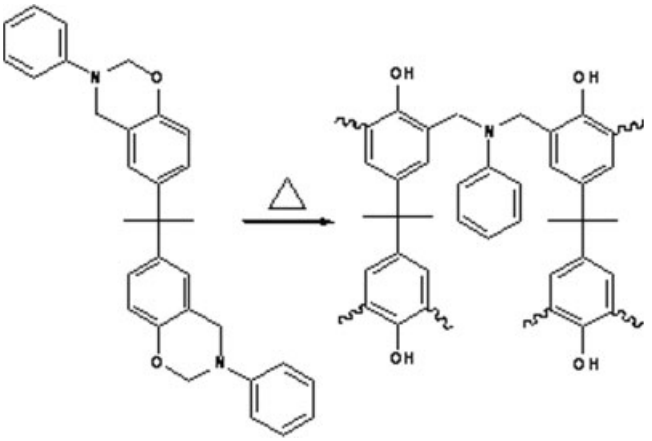

Scheme 1 Bisphenol-A based benzoxazine monomer and its polymer.

porosity and interfacial bonding between matrix and microballoon are the two major factors determining the strength of syntactic foams, and these factors have been investigated with the use of scanning electron microscopy (SEM). The dependency of mechanical properties on the composition of the foam is discussed.

EXPERIMENTAL

Materials

Bisphenol-A based benzoxazine monomer was synthesized as per a reported procedure.[23] The benzoxazine monomer undergoes thermal ring-opening polymerization. During ring-opening, —OH groups are generated which catalyze the ring-opening of other monomers. The cured polybenzoxazine structure is characterized by Mannich bridges ($—CH_2—NR—CH_2—$). The benzoxazine monomer and its cured structure are shown in Scheme 1. The as-synthesized material was used for composite preparation as it contains some ring-opened structures which accelerate the polymerization process. Glass microspheres (3M Company, St. Paul, MN) with a true density of 250 kg/m^3, bulk density of 110 kg/m^3, and an average crush strength of 5.2 MPa were used as filler. Particle size distribution: effective top size 105 μm, 10th percentile 25 μm, 50th percentile 55 μm, 90th percentile 90 μm. All the specifications of the glass microballoon were provided by the manufacturer.

Processing of syntactic foams

The procedure adopted for processing syntactic foams involved the introduction of microballoons into a beaker containing the required quantity of resin dissolved in acetone. The mixture was stirred well for the uniform dispersion of the microballoons. The contents were gently mixed, and the solvent was evaporated in a vacuum oven. The dried material was filled in a rectangular mold of 15 mm × 15 mm, and compressed to a thickness of 8 mm. The pressure required for the compression of the contents is included in Table I. It was then subjected to a cure schedule of 120°C (1.5 h), 150°C (1 h), 200°C (1 h), and finally 210°C for 3 h. The syntactic foams containing varying contents of microballoon were represented as BM1 (30% by weight/61.4% by volume), BM2 (40% by weight/68.1% by volume), BM3, (50% by weight/74.1% by volume), BM4 (60% by weight/76.3% by volume), and BM5 (70% by weight/78.0% by volume). The cure schedule was adopted based on rheological cure investigation and IR studies.[24] Syntactic foams with varying density were also fabricated, in which the weight ratio of resin to microballoon was fixed as 50 : 50, to study the effect of packing density on compressive strength. The syntactic foams with densities 272, 380, and 537 kg/m^3 were used for investigating the effect of packing density on the compressive strength. The composites were compressed to different extents to regulate the density. The pressure applied to obtain foams with density 537 kg/m^3 was slightly above the average crush strength of microballoon (5.4 MPa), and for the other two foams, the applied pressure was well below the average crush strength of microballoons.

Characterization

Mechanical properties were evaluated using a computer-controlled Universal Testing Machine, Instron 4202 model in accordance with ASTM D 790 for flexural strength (specimen size, 130 × 13 × 8 mm^3), ASTM D 3039 for tensile (specimen size, 150 × 25 × 8 mm^3),

TABLE I
The Composition of Syntactic Foams

Sample reference	Resin		Microballoon		Density (kg/m^3)	Void (air) (vol %)	Pressure applied for compaction (MPa)
	Weight (%)	Volume (%)	Weight (%)	Volume (%)			
BM1	70	29.9	30	61.4	512	8.7	4.1
BM2	60	22.0	40	68.1	434	9.9	4.5
BM3	50	16.4	50	74.1	378	9.5	4.9
BM4	40	11.7	60	76.3	330	12.0	5.3
BM5	30	8.2	70	78.0	293	13.8	5.5

and ASTM D 695 (specimen size, 16 × 8 × 8 mm^3) for compressive studies. The three-point bending test was conducted for the measurement of flexural strength with a crosshead speed of 2 mm/min and a span width of 130 mm. Tensile and compressive strength tests were conducted at a crosshead speed of 5 mm/min. All the measurements were done at room temperature. A minimum of four samples was evaluated for each mechanical property. The surfaces of specimens failed during flexural testing were examined by SEM (PHILIPS XL-30). Samples were sputter-coated with gold to impart electrical conductivity and reduce charging artifacts. The operation voltage of the SEM was 10 kV.

Since the preparation involves mechanical mixing of materials, some air entrapped in the material system could give rise to open cell structure porosity or voids. The density of the cured benzoxazine resin was determined by water displacement method and it was found to be 1190 kg/m^3. The true density (250 kg/m^3) of microballoons was used for void volume calculation.

Void volume % of the syntactic foams was calculated by using the eq. (1)

$$\text{Void volume } \% = \frac{D_{\text{theo}} - D_{\text{meas}}}{D_{\text{theo}}} \times 100$$

where D_{theo} and D_{meas} are the theoretical and measured densities of the syntactic foams, respectively.

RESULTS AND DISCUSSIONS

Porosity of syntactic foams

Syntactic foam is considered to have a three-phase structure, viz., matrix resin, cenospheres (microballoons), and entrapped air (referred as voids). During the processing of syntactic foams, some air gets entrapped within the matrix, which is termed as matrix porosity or voids. It is very important to understand the porosity of the syntactic foams since it significantly affects the material properties. The matrix porosity is undesirable as it reduces the strength of the foam and can also lead to increased moisture absorption which lowers the strength. In the processing of syntactic foams, damage to some microballoons is unavoidable. Careful processing can minimize the damage, but one cannot completely eliminate it. Further, the rupture of microballoons opens up their cavity (microballoon cavity), which can be filled with the matrix resin. Hence, fracture of microballoons leads to an increase in the density of syntactic foams. The composition of the foam, the pressure used for their compaction, density, and the void volume are compiled in Table I.

The inclusion of microballoons into the polybenzoxazine matrix diminishes the density. There is a concomitant increase in the void content also. From BM1 to BM5, the void volume increased from about 8–14%. It is seen that the density decreases from 512 to 293 kg/m^3 with the incorporation of microballoons. The increase in void content (excluding the microballoon voids) with increase in microballoon percentage can be ascribed to the occurrence of ''thin matrix layer'' or absence of matrix between microballoons when sufficient resin is not available. Usually, the microballoon may be crushed during processing exposing their own porosity, which can be occupied by the smaller microballoons or by the resin. In resin-starved situations, this possibility is ruled out, and the open vacancies generated from crushed microballoons are likely to be left as voids. Thus, the crushed microballoons act as effectively as the uncrushed ones in bringing down the density.

The air voids present in syntactic foams may be isolated or accumulated. Though both types of voids do lead to deterioration in mechanical properties, the existence of interconnected or accumulated voids is highly undesirable. A number of nonaccumulated voids present a comparatively better situation than a single accumulated void having the same effective volume. With increase in microballoon content, the possibility for interconnected void increases. In the present case, the accumulated voids are present in all composites irrespective of the percentage of resin for the reason that the present case is generally a resin-depleted one. Figure 1(a,b) shows the accumulated voids in BMI (low MB content) and BM5 (high MB content) syntactic foams. It may be remarked that a good microballoon packing is ensured by the wide particle size distribution, wherein the space between bigger microballoons is effectively filled by small-sized microballoons (see Fig. 2).

Mechanical strength of syntactic foams

The mechanical properties of syntactic foams are given in Table II. As the target of this work is the preparation of lightweight, moderate strength syntactic foams based on polybenzoxazine, relatively high volume fractions of microballoon were incorporated to the resin matrix. The content of microballoon in syntactic foams was varied from 30 to 70% by weight (61–78% by volume of microballoon). It is found that compressive and tensile strengths were optimized at about 40% by weight (68% by volume) of microballoons. Beyond this composition, these properties follow a decreasing trend. The diminishing trend is attributed to the high volume fraction of microballoon, where the layer of matrix resin between microballoons is very thin, which fails easily under stress. The lowering trend is also related to the high volume of voids pres-

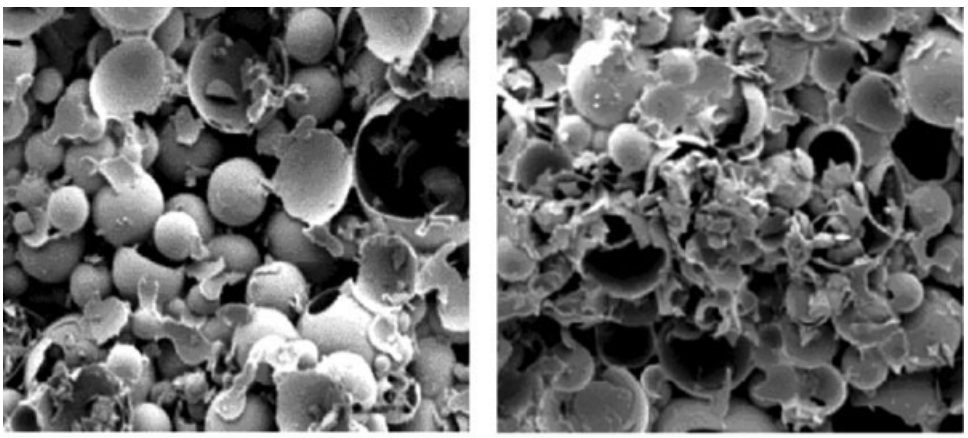

Figure 1 Accumulation of voids due to resin scarcity in (a) BM1 (×200, 100 μm) and (b) BM5 (×246, 100 μm), respectively.

ent in the systems. Gupta et al.[25] also have reported that syntactic foam containing 68% by volume of glass microballoons showed optimum compressive strength in an epoxy resin system. They used glass microballoons of bulk density 250 kg/m^3 with about 65% of microballoons below 100-μm range and the particle size distributed upto 175 μm. In our study, the density of the microballoon was 250 kg/m^3 and the particle size distribution is broader, with effective top size 105 μm, 10th percentile 25 μm, 50th percentile 55 μm, and 90th percentile 90 μm. Because of this wide particle size distribution, smaller-sized microballoons occupy the voids as explained earlier. The wide particle size distribution and density factor may be the rationale for a similar observation made by Gupta et al.[25]

Results in Table II show that tensile strength and compressive strength get optimized at the same composition (40% by weight/68% by volume of microballoon) and that the compressive strength value is higher than the tensile value. This may be attributed to the different behavior of voids under various loading conditions. It is reported that voids of a given geometry will open at a faster rate under tension than they start to close under compression load of the same magnitude.[25] Some studies[26,27] demonstrate that the mean value of the stress concentrating factor increases under tension with increase in the volume fraction of voids. This reduces the yield strength of the foam. Some amount of porous structure helps release the compressive stress.[26] However, an excess amount of pores will produce negative effects.[27] In the present work, flexural strength manifested a continuously diminishing behavior with the addition of microballoon. This partly explains the observed trends in compressive strength of the foam composites on varying the microballoon concentration. In a perfect composite, the flexural strength is expected to follow the trend of tensile and compressive strengths. Thus, it should have shown a maximum in the microballoon concentration scale. The continuous decreasing trend in flexural strength shows the influence of the air voids in deciding the property profile. The voids respond differently under different loading conditions. The trends in mechanical properties and their relation to voids will be described in the section in morphology analysis by SEM.

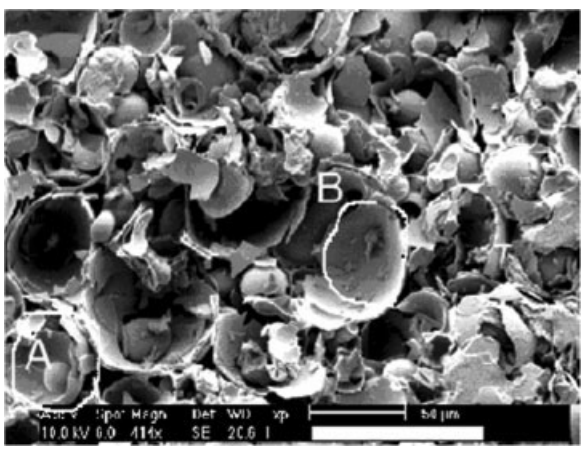

Figure 2 Small-sized microballoons occupying the open pores of crushed MBs (marked as A) and filling up of MB porosity by matrix resin (marked as B).

The average crush strength of the microballoons is 5.2 MPa. The compressive strength of compositions up to 60% by weight (74.1% by volume) of microbal-

TABLE II
The Mechanical Properties of Syntactic Foams

Sample reference	Tensile strength (MPa)	Flexural strength (MPa)	Compressive strength (MPa)
BM1	1.0 ± 0.4	3.8 ± 0.4	4.8 ± 0.6
BM2	2.7 ± 0.2	3.2 ± 0.5	7.2 ± 1.1
BM3	1.3 ± 0.3	3.2 ± 0.3	5.3 ± 0.5
BM4	1.4 ± 0.1	3.0 ± 0.4	3.0 ± 1.0
BM5	1.0 ± 0.4	3.0 ± 0.1	1.8 ± 0.3

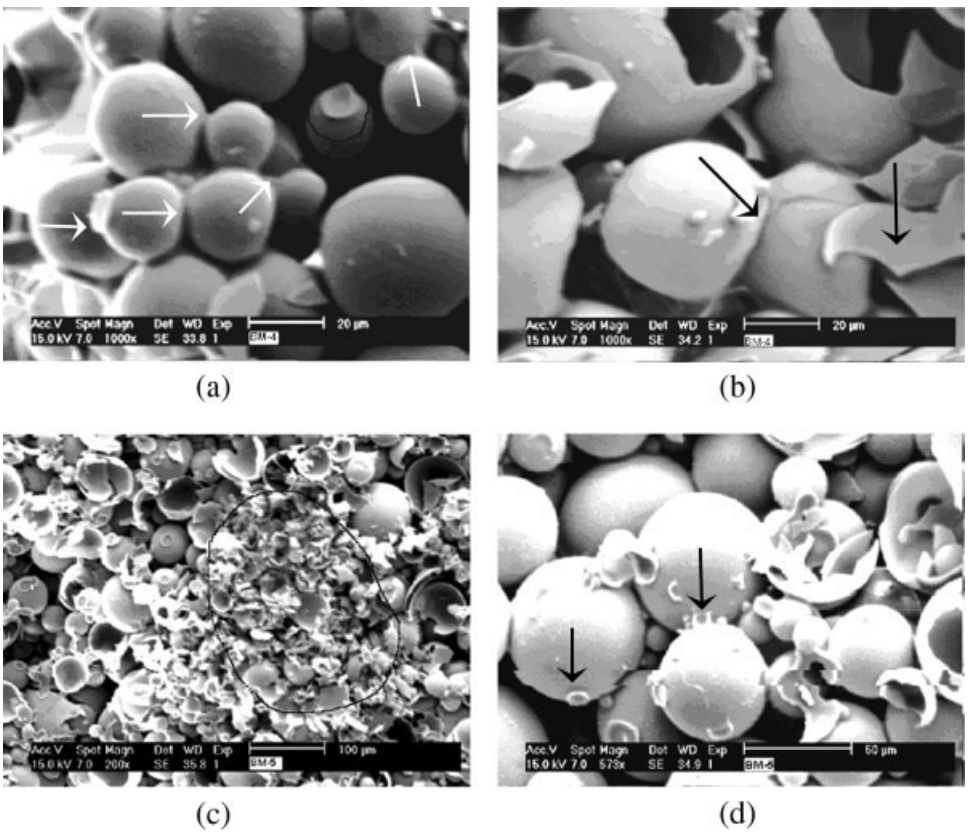

Figure 3 SEM pictures (a, b, c, d) depicting various failure features in BM4 and BM5 syntactic foams {read as a → b (top row) and c → d (bottom row)}.

loon is either very close to or above this value. But the compressive strengths of BM4 and BM5 are significantly lower than the aforementioned value. It is explained as follows. It is seen that in BM4 and BM5 compositions, the air void volume percentage is high compared to the other three compositions. At higher filling ratios of microballoon, the voids formed near individual particles begin to interact with each other. It becomes likely that the voids will merge and cause rapid specimen failure as soon as the matrix begins to separate.

Interfacial bonding between matrix and microballoons

Under flexural loading, the specimen experiences compressive force on the top part and tensile force at the lower part. It is expected that during flexure loading, failure occurs at the side under tensile stress.[28] If we consider the composition beyond BM2, the trend in properties with microballoon content is that compressive strength decreases drastically while tensile and flexural properties decreases only marginally with increase in microballoon concentration. A similarity in tensile and flexural strength profiles leads to the conclusion that the contribution of the tensile component is more significant than the compressive component in deciding the failure of the foam under flexural stress, since flexural loading is a combination of tensile and compressive loads.

The SEM analysis of various failure modes in sample surfaces failed under flexural loading will be useful to describe the observed trends in mechanical properties. It is known that the mechanical potential of a material depends mostly on the strength of polymer, filler, and adhesion between the filler and resin. The interface between filler and resin is very significant and strength could deteriorate with a weak interface. The bonding environment of the filler and the resin in a syntactic foam can be in different ways such as (i) microballoons fully in the pool of resin, (ii) microballoons partially in the resin pool (partially debonded), (iii) microballoons completely out of the resin pool (fully debonded), (iv) resin flow over the microballoons, and (v) microballoon over another microballoon (no resin–microballoon contact). Presence of voids, debonded microballoons, nonwetting of microballoons by resin, aggregations of filler, etc. are the features implying low mechanical interlocking of microballoons with the resin.

The various adhesion features that could be noticed in SEM pictures are shown in Figure 3(a–d). For comparison, SEM pictures of BM4 and BM5 foams (failed samples) containing high microballoon concentration

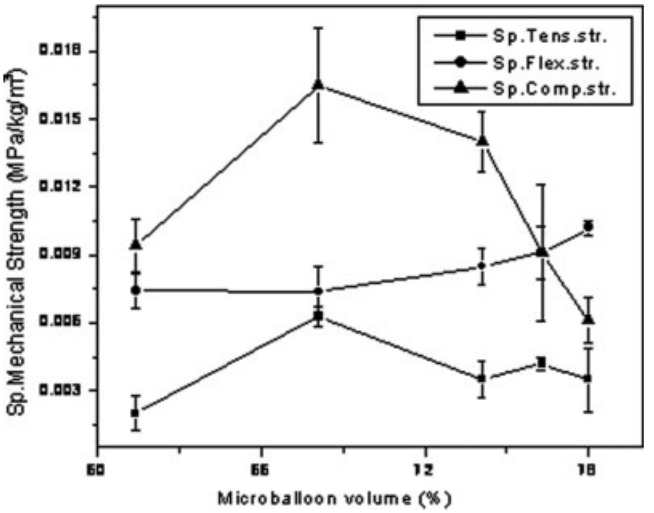

Figure 4 Variation of specific mechanical strength of polybenzoxazine syntactic foams with microballoon content.

are given. In BM4 foam, only a small region of the microballoon is in contact with other microballoons through resin [Fig. 3(a)]. In other words, in a microsphere, some region is bonded and the remaining portion is nonadhered. This feature leads to the ''multiple resin-neck formation'' (marked in figures). A good amount of voids are also observed which are created due to this phenomenon. Some voids are occupied by the smaller-sized microballoons as a result of large particle size distribution of microballoons. Because of low bonded area, the microballoons have broken away under applied stress. The broken part of microballoon is retained as a ''disc-shaped microballoon regions'' (marked in figures) on other microballoons. Regions over microballoons, where the resin is spread, can also be seen. The microballoon has been pulled out from here. These areas are the stress-concentrating loci responsible for the easy failure of the foam composites. In contrast to BM4, SEM picture of BM5 [Fig. 3(c,d)] demonstrates a sizeable proportion of damaged microballoons because of the higher stress used for compaction. The nonuniform wetting and consequent debonding of microballoons are more severe in this case. Further reduction in resin proportion (*vis-à-vis* BM4) causes segregation of microballoons (resin-starved). This phenomenon has a catastrophic effect on mechanical properties. The features such as resin-neck formation and disc-shaped microballoon regions appear more frequently in the microballoon-rich systems (e.g. BM5). It is possible that these two phenomena act cooperatively to lower the strength of BM5 in comparison to BM4.

Specific mechanical strength of syntactic foams

Specific mechanical strengths (strength/density) are plotted against microballoon volume percentage in Figure 4. The specific tensile strength (SpT) of syntactic foams showed an initial increase (upto 68% by volume of microballoons) followed by a diminution. The values get stagnated beyond 74% by volume of microballoons. The diminution in SpT on increasing filler content indicates that the relative reduction in strength is higher than that in density. It can be concluded that about 40% by weight (68% by volume) of microballoons imparts the maximum SpT to the syntactic foams.

Specific compressive strength (SpC) of syntactic foams also increases up to 40% by weight (68% by volume) of microballoons and exhibits a steep decrease beyond that composition. On the other hand, specific flexural strength (SpF) exhibited a continuous increase. It is remarkable that the variation in flexural strength with density is not significant (Table II). As the flexural strength does not vary much with diminution in density, the SpF showed an increasing trend.

Effect of packing density on compressive strength

Since density is a critical factor in determining the applicability of the material for certain areas, the dependency of compressive strength on packing density was examined. For this, syntactic foams with densities 272, 380, and 537 kg/m^3 were processed (keeping resin-to-microballoon ratio as 50 : 50 by weight). For this weight ratio, the maximum density attainable is 400 kg/m^3 (theoretical), provided the volume fraction of voids is zero. But a sample with final density of 537 kg/m^3 was obtained for which the density is well above the limiting value of 400 kg/m^3. This requires a compaction pressure greater than the average crush strength of microballoons. The compaction pressure is shown in Figure 5. This would mean that a good proportion of microballoons has been crushed during

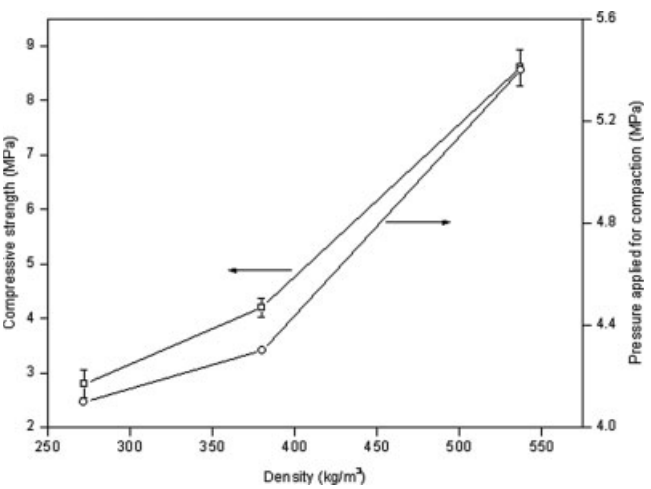

Figure 5 Relationship among compaction pressure, compressive strength, and density of foams (resin-to-microballoon ratio is 50 : 50 by weight).

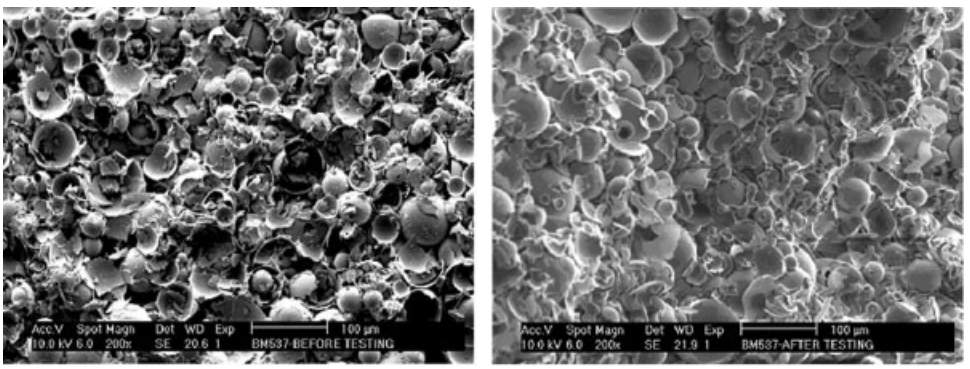

Figure 6 Crushing of microballoons in BM-537: (a) before testing and (b) after testing.

compaction, and the final material contains some particulate glass material. Hence, a fracture analysis of sample having density 537 kg/m^3 was done. The top surface of the material was analyzed before and after testing. The crushing of microballoons during molding is quite obvious [Fig. 6(a)]. After testing, the proportion of crushed microballoons increased [Fig. 6(b)]. This high level crushing of MBs is the basis for a rise in density beyond the theoretical value. Compressive strength variation of the resultant syntactic foams is depicted in Figure 5. The strength is proportional to the density. The compressive strength increased from $\sim$ 3 MPa (for density 278 kg/m^3) to $\sim$ 9 MPa (for density 537 kg/m^3). It is obvious that the microballoons have a major role in load bearing and has a profound effect on compressive strength.

These observations imply the potential of polybenzoxazine-based syntactic foams for use as moderate strength, lightweight structures. Since polybenzoxazine is basically a phenolic resin, these composites could be a potential candidate for lightweight thermostructural applications as in ablative thermal insulation.[29]

CONCLUSIONS

This work is focused on the preparation and investigation on the mechanical properties of the hollow glass microspheres-filled polybenzoxazine syntactic foams. Associated with a diminution in specific gravity, the void percentage of syntactic foam increased with an increase in microballoon content. The voids exhibited the tendency to get accumulated. The tensile and compressive strength got optimized $\sim$40% by weight (68% by volume), whereas flexural strength exhibited a general decreasing trend with increase in microballoon content. Good compressive strength was displayed by the foams, thanks to the good load-bearing ability of microballoons. The strength increases on crushing the microballoon and filling the pores with broken pieces or resin. The SpT and SpC optimized at 68% by volume of microballoons, whereas SpF showed a continuous increase with increase in microballoon content. The features like multiple resin-neck and disc-shaped region formation have been displayed by the syntactic foams. The exposed porosity of the microballoons during compaction gets occupied by the smaller-sized microballoons because of wide particle size distribution. The crushing of microballoons during molding and testing was inevitable for composition, with specific gravity beyond the theoretical values. The failure in lower-density foams was controlled primarily by the fracture of microballoons. The experimental campaign confirmed the remarkable potentialities of the polybenzoxazine syntactic foams for use as low-density, moderate strength structural and thermostructural materials.

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