

Silica Fiber–Polybenzoxazine–Syntactic Foams; Processing and Properties

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ABSTRACT: Polybenzoxazine filled with chopped silica fibers and their syntactic foams of varying composition and densities were processed. The composition and density variations were achieved by regulating the relative concentrations of silica fiber and glass microballoons (MB). The variation of tensile, compressive, and flexural properties with change in composition was investigated. For the silica-fiber filled materials, the property attained a maximum at about 40% volume content of fiber, and thereafter, the properties showed a diminishing trend. The incorporation of microspheres significantly lowered the strength of silica filled materials. However, the decrease in the specific flexural strength was less pronounced and the strength was unaffected beyond a certain microsphere content. During processing and mechanical testing, a large quantity of fibers was fractured, which reduced the strength of silica filled systems. The diminution in material strength on embedding microspheres is attributed to the

presence of stress concentrating loci as evidenced from SEM analysis. The various factors leading to the property variation with composition are discussed with microscopic analyses, like clustering of fibers, crack propagation, fiber pull out, and debonding of fibers from resin phase. Dynamic mechanical analysis revealed an improved damping property for the filled materials in contrast to the unfilled polymer. The T_g (deduced from $\tan \delta$ maximum from DMTA) decreased in silica fiber containing materials and on incorporating the MB, the values reverted back to that of the neat polymer. Both silica and MB conferred better thermal and thermooxidative stabilities to the polybenzoxazine. However, the degradation mechanism is nonoxidative in nature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1091–1099, 2008

Key words: polybenzoxazine; filled materials; syntactic foams; mechanical properties

INTRODUCTION

Fiber composites play an important role in the aerospace industry and they are used as primary structures in commercial and military aircraft.^{1,2} Phenolic composites provide some good characteristics like flame retardation, low smoke generation, and fairly high temperature resistance. Carbon and silica–phenolic composite systems are also good candidates as ablatives. However, some shortcomings of phenolic resins such as release of by-products during cure, formation of voids, and limited shelf life etc. is obviated in polybenzoxazines due to addition cure. In this context, polybenzoxazine as a new generation of phenolic resins gains attention because of many advantages such as near zero shrinkage upon polymerization, no need of catalyst for polymerization, good thermal stability and mechanical strength, and very low moisture absorption.^{3–7} Hence, polybenzoxazine composites are potentially important. Polybenzoxazines are derived from the ring-opening poly-

merization of benzoxazine monomers. Fiber-reinforced composites of thermosets are needed as load bearing structural components in aerospace field because of superior strength and damage tolerance.⁸ Polybenzoxazine belonging to phenolic family, its silica composite/filled materials could serve as potential ablative thermal protection systems. Low-density silica composites will be preferred as lightweight thermal protection systems. There has been very little work on polybenzoxazine composites.^{9–12} No report is available on low-density composites of polybenzoxazine.

Syntactic foams are composites consisting of hollow microspheres that are dispersed in a resinous matrix and have been used as structural components.^{13–16} They possess low density with high stiffness and moderately good compressive strength.^{17–19} Typical applications for syntactic foams are as automotive tooling compounds, ablative heat shields for re-entry vehicles, underwater buoyancy aids, and structural components in submarines and missiles. They are used for protective structural components as they reduce the damage and prevent failure of other components by introducing their own failure. Syntactic foams of cyanate esters, epoxies etc. have been investigated for thermal protection system in aerospace applications.^{20,21} Different failure modes

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in syntactic foams have been reported.²² To our knowledge, there are few studies on such composites based on polybenzoxazine.

The main objective of this study is to develop a low-density syntactic foam of polybenzoxazine containing silica fiber as filler material, i.e., fiber-embedded polybenzoxazine syntactic foams. Syntactic foams have the real advantage of being fabricated over a large density range and possessing useful mechanical properties due to the presence of hard glass MBs. A noteworthy benefit of MBs is that they can lower the density while possessing good mechanical and thermal properties. Regarding the introduction of fibers into such foams, those in the form of chopped strands may improve the stiffness of the material. This article describes the processing of silica fiber containing polybenzoxazine and its syntactic foams. Their mechanical and thermal properties have been examined as a function of filler and fiber content. SEM analysis was used to examine the fracture surface of composites/filled materials. The results are valuable inputs for design of fiber containing syntactic foams based on polybenzoxazine for possible thermostructural applications.

EXPERIMENTAL

Materials

Bisphenol-A based benzoxazine monomer was synthesized as per a reported procedure.²³ The as-synthesized material was used for composite preparation since it contains some ring-opened structures, which will accelerate the polymerization process. Glass microspheres were supplied by 3M company (USA) with a true density of 250 kg/m³ were used as closed pore fillers. These MBs have crush strength of 5.2 MPa as provided by the manufacturer. Silica fibers (with >98% silica content) in the form of chopped strands of fiber length 7–10 mm and fiber diameter 12 μm were supplied by Valet High Tech Composites, Chennai, India and were used without any sizing agent.

Preparation of polybenzoxazine containing silica-fiber

Fiber filled polybenzoxazine with various fiber contents were processed. Benzoxazine monomer was dissolved in acetone and the fiber was added in stages to achieve effective wetting of the resin with fibers. The contents were gently mixed and the solvent evaporated in a vacuum oven. The dried material was filled in a rectangular mould and subjected to a cure schedule of 120°C (1.5 h), 150°C (1 h), 200°C (1 h), and finally 210° for 3 h. Appropriate quantities of resin and fiber were used to obtain the

TABLE I
Details of BS and BSM Filled Systems

Reference	Volume percentage			Void	Density (kg/m ³)
	Bz	SF	MB		
BS1	61.1	30.4	---	8.5	1298
BS2	56.5	38.5	---	5.0	1345
BS3	36.1	54.2	---	9.7	1490
BS4	28.5	62.9	---	8.6	1561
BSM0 (BS2)	56.5	38.5	---	5.0	1345
BSM1	30.7	19.8	36.5	13.0	879
BSM2	24.4	15.9	46.8	12.9	691
BSM3	19.8	11.9	56.9	11.4	614
BSM4	16.9	10.2	64.1	8.8	562
BSM5	13.9	9.1	68.9	8.1	507

Bz, Benzoxazine; SF, Silica fibre; MB, Microballoon.

desired dimension for the cured block (10 × 10 × 0.5 cm³). The resin and fiber volumes were calculated by taking the density of resin as 1.2 g/ml (true density) and that of silica fiber as 2.0 g/ml (true density). Material composition details are given in Table I. The cure schedule was adopted based on a rheological cure investigation²⁴ and FT-IR analysis. The blocks were cut into desired size according to ASTM D-790 (5 × 13 × 100 mm³) for flexural strength, ASTM D-3039 (5 × 13 × 69 mm³) for tensile, and ASTM D-695 (5 × 5 × 10 mm³) for compressive property evaluation.

Preparation of polybenzoxazine–silica fiber–syntactic foams

To prepare syntactic foams of polybenzoxazine containing silica fiber, a fiber-resin composition corresponding to BS2 (refer Table I) was taken. To this, the MB was added in different proportions, viz: 10% (BSM1), 20% (BSM2), 30% (BSM3), 40% (BSM4), 50% (BSM5) by weight. Initially, fibers were added to the resin solution and allowed to be wet by the resin. Thereafter, the filler was added to the mixture, gently mixed, and the solvent was evaporated. Subsequently, a procedure similar to that adopted for the preparation of fiber filled materials of polybenzoxazine was followed for compression and curing. The cured blocks were cut into desired dimensions for tensile, compressive and flexural tests.

Characterization

Mechanical properties were measured in a computer controlled Universal Testing Machine, Instron 4202 model. The three point bending test was conducted for the flexural strength measurement (gauge length = 80 mm) with a crosshead speed of 2 mm/min. Tensile (gauge length = 10 mm) and compressive strength testing (gauge length = 5 mm) were con-

ducted at a crosshead speed of 5 mm/min. All the measurements were taken at room temperature. A minimum of four specimens were analyzed for each case. Thermomechanical analysis was conducted to obtain coefficient of thermal expansion by using a Perkin Elmer TA7 instrument. Dynamic mechanical measurements were conducted on a Rheometrics Scientific model Mark IV (UK) at a frequency of 1.0 Hz and a heating rate of 10°C/min in bending mode. The flexurally failed surfaces of samples were coated with a conductive layer of gold using a sputtering unit and subjected to SEM analysis (PHILIPS XL-30). Void volume of the prepared materials was calculated using Eq. (1).

$$V_{\text{voids}} = V_{\text{slab}} - [V_{\text{resin}} + V_{\text{fiber}} + V_{\text{microballoon}}] \quad (1)$$

$$V_{\text{component}} = W_{\text{component}}/d_{\text{component}} \quad (2)$$

where V_{voids} and V_{slab} represent the volume of the voids and slab, V_{resin} , V_{fiber} , and $V_{\text{microballoon}}$ represent the volume of each component used for material preparation. The volume of each component is determined by Eq. (2) where $W_{\text{component}}$ is the weight of component in the filled materials and $d_{\text{component}}$ is the density of the component. True densities were used for the calculation of voids. The components of silica fiber-polybenzoxazine systems are resin and silica fiber whereas those of silica fiber-polybenzoxazine-MB systems are the resin, silica fiber, and MBs. The quantities and densities of the respective components were considered for calculation of voids.

RESULTS AND DISCUSSIONS

Mechanical properties of filled systems

Details of the density and composition of silica fiber-polybenzoxazine and silica fiber-MB-polybenzoxazine systems are given in Table I. From BS1 to BS4, the material density increases as the fiber composition increases. The measured density of syntactic foam is lower than the theoretical one implying the presence of voids in the filled materials. The void content also tends to increase on adding more fiber.

The tensile strength is the ability of the material to oppose stretching force, compressive strength is the resistance of material over compression, and flexural strength is the ability to withstand a bending force. Hence these mechanical forces are very important for practical uses. The properties for the various compositions are given in Table II. For fiber-filled materials, the tensile strength increases with fiber content and maximises at BS2 composition in the series investigated. Compressive and flexural strength also showed an increasing trend with fiber content up to BS2 composition. The variation in property

TABLE II
Mechanical Properties of BS and BSM Systems

Reference (cured)	Tensile strength (MPa)	Flexural strength (MPa)	Compressive strength (MPa)
BS1	26.5 ± 3.0	63.3 ± 4.6	111.0 ± 23.7
BS2	36.0 ± 4.3	75.7 ± 6.4	116.8 ± 17.5
BS3	35.8 ± 3.5	72.2 ± 2.3	110.6 ± 6.1
BS4	15.8 ± 1.6	40.7 ± 6.4	63.0 ± 15.5
BSM0 (BS2)	36.0 ± 4.3	75.7 ± 6.4	116.8 ± 17.5
BSM1	8.1 ± 0.1	16.0 ± 6.2	30.0 ± 11.3
BSM2	7.4 ± 0.2	10.0 ± 0.1	28.0 ± 13.5
BSM3	4.6 ± 0.9	8.5 ± 2.5	20.5 ± 8.3
BSM4	2.5 ± 0.9	7.7 ± 0.1	15.9 ± 5.2
BSM5	2.1 ± 0.8	5.9 ± 1.1	6.8 ± 2.2

among materials of different fiber composition is not very significant. Moreover, the filled systems showed no enhancement in properties vis-à-vis the neat system [Flexural strength and tensile strength are 90–100 MPa²⁵ and 30–40 MPa,²⁶ respectively and reliable compressive strength value is not obtained/available due to the brittleness of the neat polymer]. The load carrying ability of fiber determines the mechanical strength of a composite/filled material. Both the fiber and matrix carry a part of the applied load as a function of their relative stiffness and volume fraction. If the adhesion between fiber and matrix is weak, the mechanical properties will not be high. As the continuity of the matrix is lost, the fiber filled materials show lower strength than the unfilled matrix. The voids catastrophically reduce the strength of composites/filled material. As the filled systems showed a diminution in strength, it points to the possibility for poor resin wetting, non-homogeneity, void formation, etc. In general, voids do indeed have an adverse effect, which is more pronounced for the tensile and flexural than compressive forces. Voids can thus lower the tensile and flexural strength of materials. All these features are observed in SEM analysis and discussed later.

Tensile modulus of the silica filled polybenzoxazine materials are plotted against silica fiber content in Figure 1. The tensile modulus of neat resin is about 3GPa. All silica filled materials exhibited higher moduli compared to neat value. BS2 showed the highest value about double that of the unfilled resin. The stress-strain curves of silica filled polybenzoxazine materials are shown in Figure 2. All BS materials exhibited elastic deformation and a sudden break at maximum stress. No plastic deformation was observed.

It is understood that silica fiber filled material did not exhibit enhancement in mechanical strength vis-à-vis the neat matrix. A similar observation has been reported in a previous work wherein the fiber com-

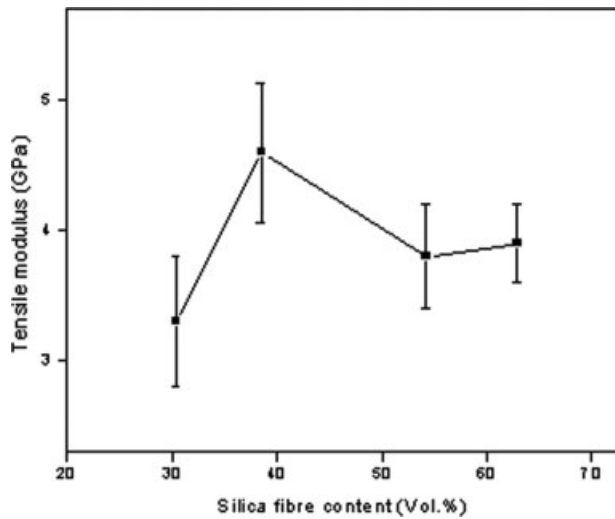


Figure 1 Tensile modulus variation with silica fiber content (BS).

posites exhibited lower mechanical strength than the neat polymer.²⁷ This was correlated to microscopic failure mechanism detected by SEM of the fractured surfaces and was attributed to the poor fiber–matrix bond strength occurred in such fiber composites. The mechanical adhesion is a key factor in determining the mechanical strength of the composites.²⁸ Similarly, fly ash containing (about 60% silica) reduced the strength of fiber reinforced epoxy composites.²⁷ This indicates the “filler effect” of silica powders, in reducing the strength of the matrix. The fractured surfaces of the fiber composites were analyzed microscopically. Matrix-fiber adhesion interaction is an important parameter that determines the strength of composites. Generally silica laminates provide a poor interface with phenolic as evident from the poor interlaminar shear strength.²⁹ During flexural

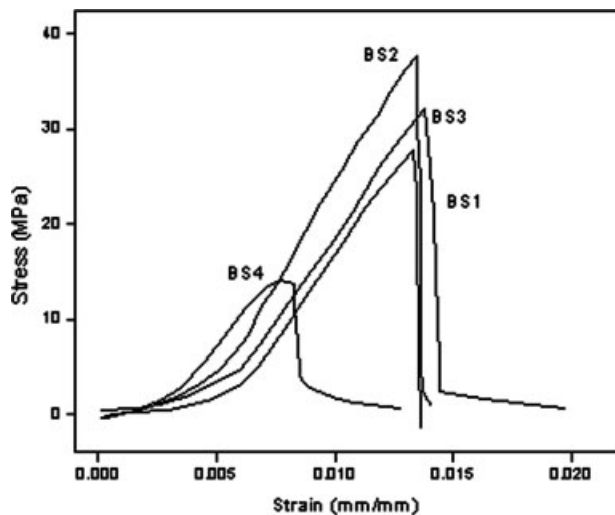
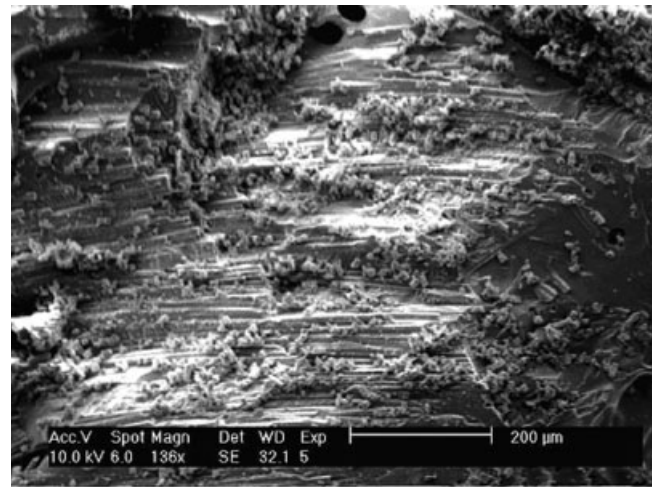
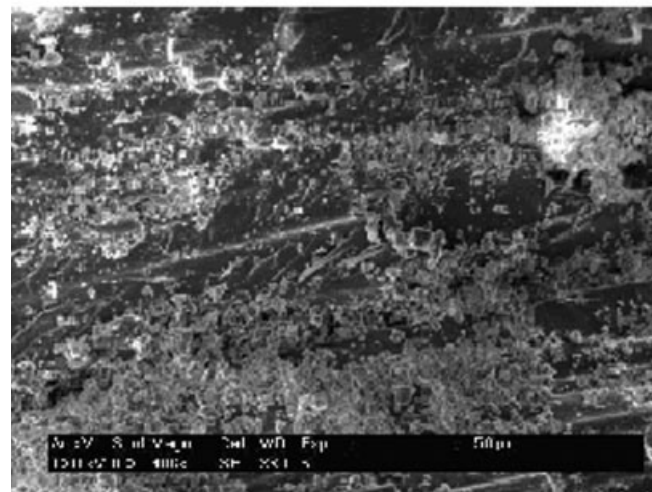


Figure 2 Stress–strain curves of BS systems.



(a)

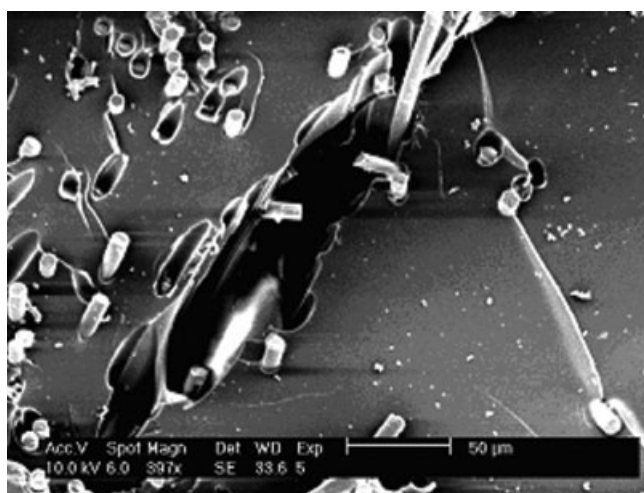


(b)

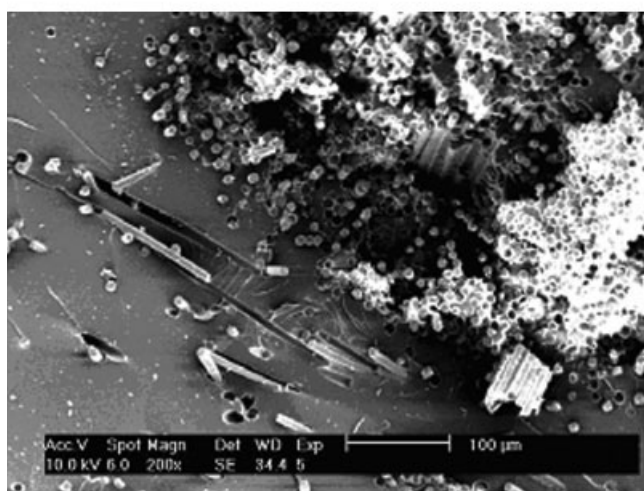
Figure 3 (a) SEM evidence for fiber wetting (b) presence of broken fibers/powdered fillers (BS2).

loading, the specimen is subjected to compressive stress on the top part of the specimen and to tensile stress at the lower part of the specimen. Hence, examining flexurally failed samples will give a better idea regarding failure modes.

As discussed earlier, the flexural strength of fiber filled materials optimized at BS2 composition and decreased thereafter. In BS2 materials, powdered silica fibers can be seen (Fig. 3). The wetting of the fibers was also observed in BS2 materials (Fig. 3). The silica fibers are very brittle and may get powdered during mixing and testing. In effect, the powdered silica fibers act as a filler and reduce the mechanical strength. In BS-1 materials possessing more resin, islands of resin are seen. The high concentration of resin causes the wet fibers to agglomerate, causing the island formation of resin, which also reduces the strength (Fig. 4). The lower magnification micrograph shows the debonding of fiber from



(a)



(b)

Figure 4 (a) Resin cracking and debonding (b) fiber clustering (BS1).

the matrix. A phenomenon of brush-like appearance of debonded fibers indicates relatively poor fiber-resin interaction. The crack propagation in the matrix can also be seen in Figure 4(a). The fiber clusters are loci for air-void entrapment and potential weak points. Probably, BS2 is the appropriate resin/reinforcement ratio, which ensures uniform wetting of fiber [Fig. 4(b)].

Fiber filled systems viz: (BS2) was considered for syntactic foam preparation since this formulation has lower density, low void content, and better strength and modulus compared to the rest in the series investigated. Moreover, its specific strength (strength/density) is higher than that of BS3. For these reasons, this composition was selected for further study. The details of fiber-syntactic foam are given Table I. (It was prepared by adding MBs to BS2 composition hence the volume percent was calculated by includ-

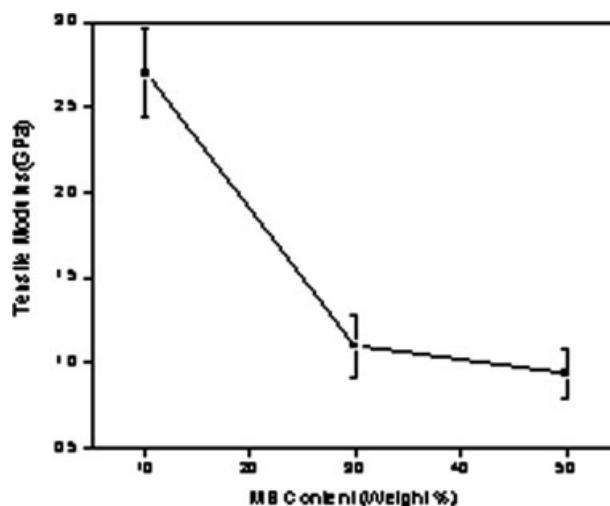


Figure 5 Tensile modulus variation of BSM systems with MB concentration.

ing the composition of MB such that the total volume is 100%, which includes volume of fiber, resin, MB, and voids). In silica-MB materials, from BSM1 to BSM5 tensile, compressive and flexural strength exhibited a continuous diminishing trend. This is expected as the high volume fraction of microspheres renders the layer of matrix resin between MBs very thin which tends to fracture easily under stress. Introduction of lower strength MB fraction could also increase the inhomogeneity of the materials. According to the basic law of mixtures for composite materials, incorporation of high quantity of lower strength fillers usually reduces the strength of the composites. The tensile modulus of MB added systems are shown in Figure 5. The MB system showed low modulus. Tensile stress-strain curves are depicted in Figure 6. No special features were observed, but with increase in MB content a tend-

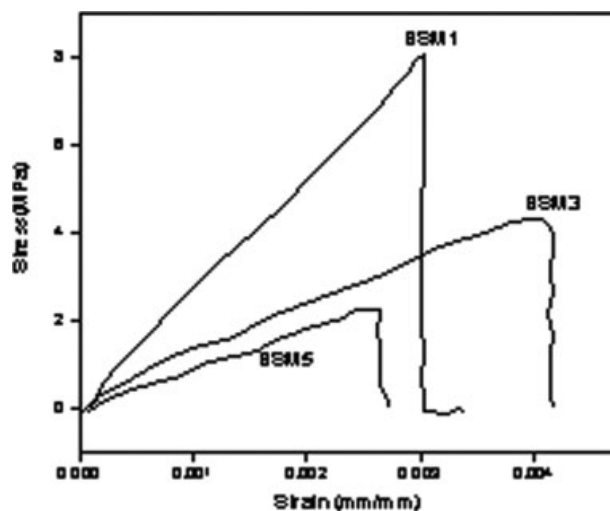


Figure 6 Tensile stress-strain curve of BSM materials.

ency for plastic deformation was observed in BSM3 and BSM5 filled materials. This can be ascribed to the breaking of MB prior to the ultimate failure.

It can be concluded that the matrix and fiber serve as load bearing components whereas the inclusion of microspheres offer predominantly weight saving because of their lower density. Obviously, the fiber filled polymer showed high load-bearing capacity compared to their syntactic foams. However, the potential for greater damage tolerance and higher energy absorption capacity will be enhanced in the fiber-containing syntactic foams.

The micrographs of silica fiber loaded syntactic foams are given in Figures 7 and 8. The SEM pictures (Fig. 7) confirmed a less ordered distribution of MB and voids in the matrix of BSM1 system. Figure 8 represents SEM photographs of BSM3 having lower flexural strength. Broken and agglomerated MBs can be seen [Fig. 8(a)]. The flexural strength diminution with MB loading can also be attributed to the poor matrix-MB bond. At high MB loading, the agglomerated MBs and fibers tend to be separated from each other [Fig. 8(b)]. It is known that the incomplete wetting of microspheres by resin could make the interface region to be filled with pockets of air, which could open during flexural loading.

Specific mechanical strength of filled materials

Though the addition of MB reduces the strength, there is also a consequent decrease in density. Since one of the objectives of the work is to derive low-density filled materials, it is of interest to consider the specific properties as well. Specific mechanical strength is the ratio of mechanical strength of the material to its density. Specific properties (strength/density i.e., properties normalized to the mass) allow for the comparison of the performance of fiber-rein-

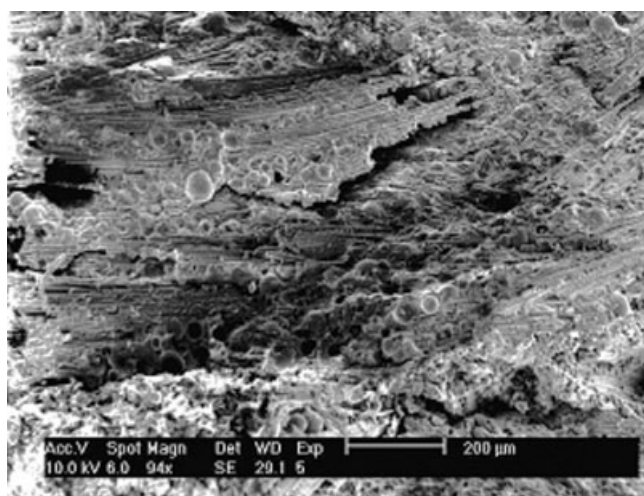
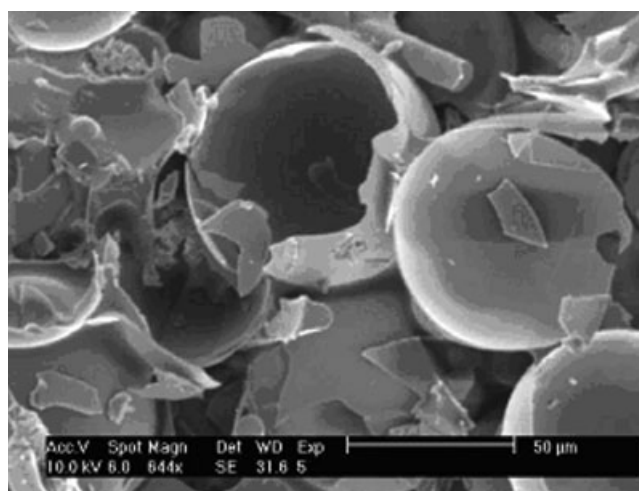
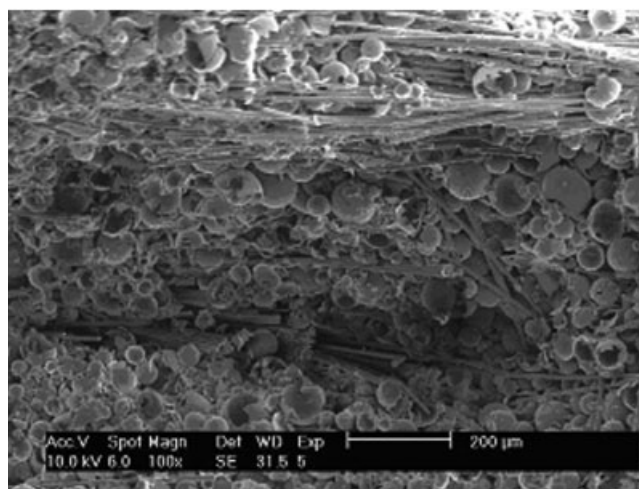


Figure 7 Distribution of MBs (BSM1).



(a)



(b)

Figure 8 (a) Debris of MBs (b) fiber-MB “interlinks” (BSM3).

forced syntactic foams to the silica filled materials. The variations in specific mechanical strength of BS and BSM composites are shown in Figures 9 and 10, respectively. Since the gain in strength is proportional to the fiber loading (and the density), the specific strength shows a general decreasing trend for the silica filled materials. This also justifies the selection of low fiber system for further modification with MB.

In MB embedded materials, specific tensile strength enhanced upon inclusion of microspheres up to about 47% by volume of MB, beyond which, a decreasing trend was observed. This happens since the relative reduction in strength is larger than that in density as reported in a previous study.³⁰ Specific compressive strength also followed a similar trend. For the low-density materials, the specific flexural strength decreases marginally and practically stag-

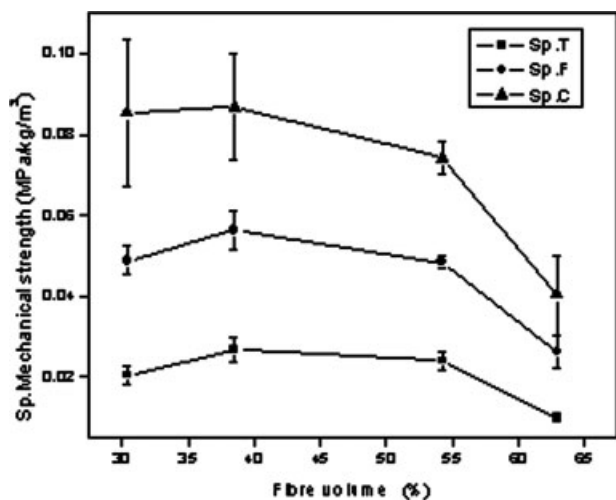


Figure 9 Specific mechanical strength of polybenzoxazine filled with silica fibers.

nates beyond 57% volume of micro spheres. It can be concluded that a composition with about 55 vol % of MB is good enough for moderate load bearing thermostructural applications (low density moderate strength materials) without great penalty on mass. Such systems are advantageous for use as thermal protection of satellites while entering the atmosphere.

Coefficient of thermal expansion (CTE)

Since syntactic foams can be used for thermal insulation of other structures, CTE is an important parameter for determining the suitability of the composites for a given substrate. The coefficient of thermal expansion for silica fiber filled materials for the temperature range 40–100°C decreased with fiber load (Fig. 11). The CTE of cured polybenzoxazine was 50–60 ppm/°C. The CTE of fiber filled materials were in

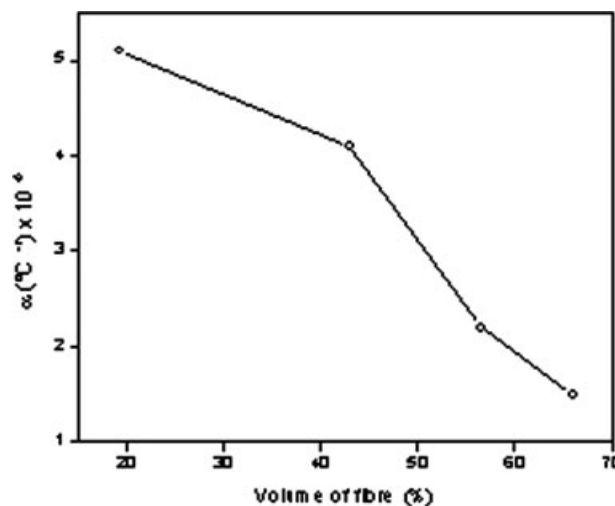


Figure 11 Coefficient of thermal expansion of silica fiber incorporated polybenzoxazines (BS).

the range (15–50 ppm/°C). Meanwhile, the coefficient of thermal expansion of all silica filled syntactic foams was still lower about 4.7 ppm/°C and showed no change with MB incorporation. Higher CTE values are observed in fiber filled materials, as the fiber is incapable of preventing the expansion of the matrix. This is indicative of a weak fiber-matrix interphase. The presence of voids, lower density etc. also accounts for the enhanced CTE of these materials. It is also seen that void volume is higher in fiber filled systems compared to fiber filled syntactic foams. The spherical MBs in fiber reinforced syntactic foams restrict the movement of matrix and as a whole the dimensional change decreases and consequently CTE value diminishes. These results show that the fiber-embedded syntactic foams have better dimensional stability under thermal stress conditions than the corresponding fiber incorporated polybenzoxazine.

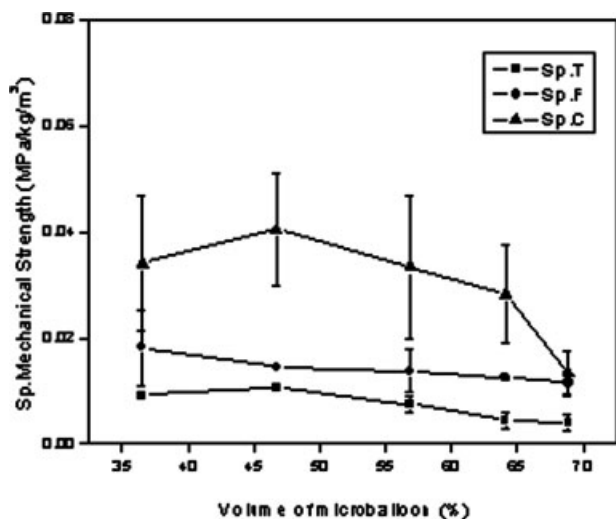


Figure 10 Specific mechanical strength of BSM systems.

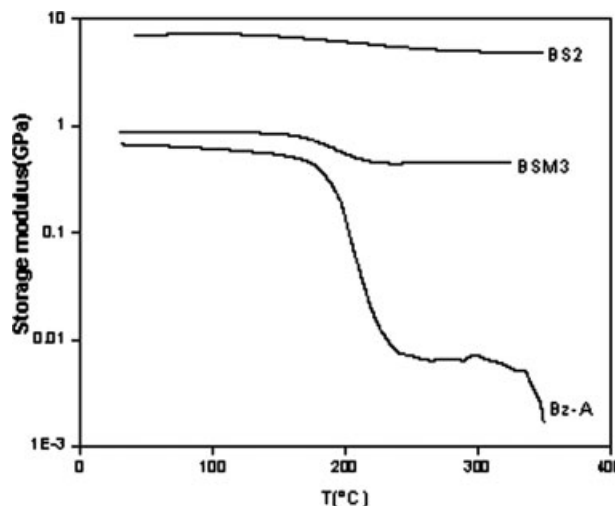


Figure 12 Storage modulus curves of BS and BSM materials.

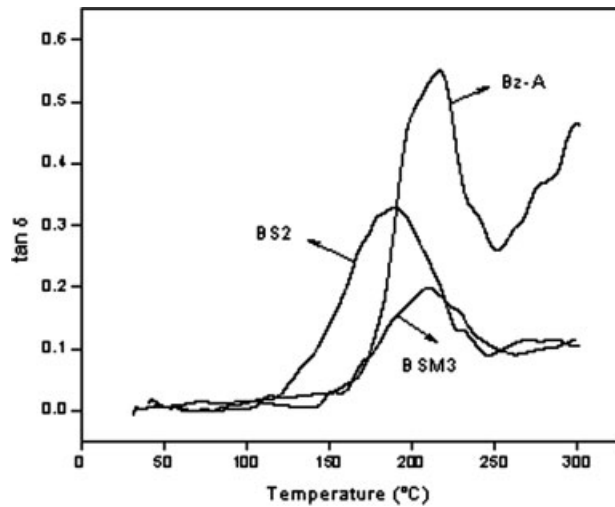


Figure 13 Variation of loss factor with temperature.

DMTA analysis

Figure 12 shows the storage modulus of silica and MB filled polybenzoxazine with increase in temperature. The storage modulus of BS2 at ambient temperature is considerably higher than that of neat resin. It can be seen that the storage modulus decreases with the introduction of MB. These observations tally with the mechanical property trends. The T_g of the materials was obtained from $\tan \delta_{\max}$ (Fig. 13). The T_g of the neat polybenzoxazine was found to be 215°C. This decreases marginally on the introduction of silica fibers and reverted back to the original value on MB incorporation. The T_g is higher for the MB added systems and it increases with MB content. This is due to the effect of the MBs that affect the mobility of the polymeric chains in the interphases between the matrix and the MBs.³¹ The lowering of T_g for BS2 may be due to the weak interphases between fibers and polybenzoxazine. The foam materials used for external thermal protection of launch vehicle is subjected to severe vibration during the launching maneuver. Hence their damping characteristics are also of importance.

The dynamic mechanical behavior of various materials was examined with reference to their loss factor. Tan delta is the damping factor, it is a measure of the ratio of energy dissipated as heat to the maximum energy stored in material during one cycle of oscillation. The capability of the polymer or

TABLE III
Height and Width at Half Height of $\tan \delta_{\max}$ in Comparison to that of Neat Polymer

Reference	Tan δ_{\max} (height)	Width at half height (°C)
Cured Bz-A	0.55	57.2
Cured BS2	0.33	67.1
Cured BSM3	0.20	73.2

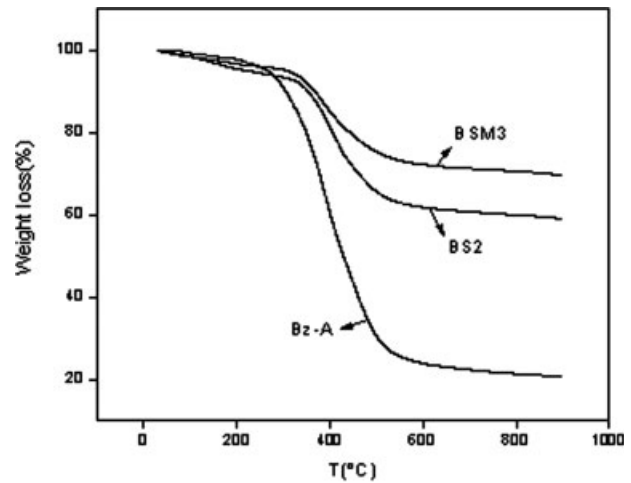


Figure 14 Comparative thermogram of filled systems in N₂.

a composite to dissipate the vibrational mechanical energy into heat depends on the intensity and broadness of the $\tan \delta$ peak at the applying temperature. To obtain material useful for damping applications, the damping peaks should be broadened. The damping behavior of composites is affected by (a) friction between polymer chain and filler, (b) friction between filler and filler (c) the deformation of MBs and nature of polymers. Hence an investigation on the damping behavior of these composites is pertinent. It can be seen from Figure 13 that the width at half height of $\tan \delta$ curve of the filled materials is enhanced compared to those of neat polybenzoxazine. The increased width indicates the ability of composites/filled materials in dissipating energy through molecular motion.

The maximum loss factor heights are 0.33, 0.2, and 0.28 for BS2, BSM3, and BSM5, respectively. The results are compiled in Table III. The broadening of damping portion by high concentration of the

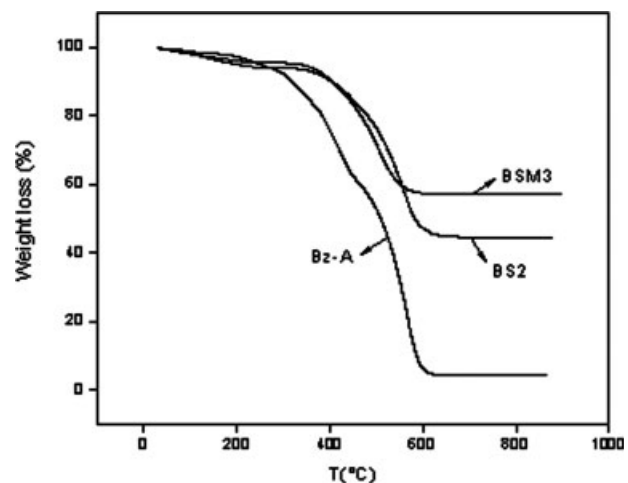


Figure 15 Comparative thermogram of filled systems in air.

TABLE IV
Initial Decomposition Temperature (T_{id}) of Filled Systems

Sample references	T_{id} (°C)	
	N ₂	Air
Cured Bz-A	311	328
Cured BS2	350	372
Cured BSM3	330	368

low-density fillers is apparent. Fillers generally broaden or lower the slope in the transition region.³²

Thermal and thermooxidative stability

Thermograms of the different filled systems were analyzed in air and N₂. They are shown in Figures 14 and 15. An increase in initial decomposition temperature (T_{id}) of the silica and silica-MB systems is indicative of the thermal stabilization effect of the filler on the polymer. This enhancement is observed both in air and N₂. Therefore, it can be concluded that the fillers confer thermo-oxidative stability to the resin. The initial decomposition temperatures (T_{id}) are compiled in Table IV. Interestingly, the T_{id} values are higher in air than in N₂. This shows that the degradation is nonoxidative in nature.

CONCLUSIONS

Polybenzoxazine based silica fiber filled materials and syntactic foams containing silica fibers were prepared and their mechanical and thermal properties were studied. For fiber filled materials, the property optimum was observed at about 40% by volume content of the fiber. Addition of MBs to the fiber filled materials decreased density as well as the strength. However, the decrease in specific strength was only nominal. The enhancement in void content with increased load of MBs or silica fiber resulted in poor strength. Fiber debonding, dewetting of fibers, and fiber cluster formation are further reasons for mechanical failure which were manifested in SEM analysis. The SEM features corroborated the trend in mechanical properties. CTE of the silica containing materials decreased with inclusion of MBs. DMA revealed the improvement in damping property of the filled materials particularly in the foam systems. The thermal and thermooxidative stability were enhanced with the incorporation of silica and MBs into polybenzoxazine matrix and the degradation is observed as nonthermooxidative in nature. By appropriate manipulation of fiber and MB composition it is possible to obtain low-density, moderate strength, polybenzoxazine materials for high temperature structural and thermostructural applications.

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