J Mater Sci (2007) 42:5398–5405
DOI 10.1007/s10853-006-0778-0

Effect of low-density filler on mechanical properties of syntactic foams of cyanate ester

Bibin John · C. P. Reghunadhan Nair · K. Ambika Devi · K. N. Ninan

Received: 20 December 2005 / Accepted: 10 August 2006 / Published online: 31 March 2007

Abstract Syntactic foam composites of cyanate ester with varying volume fractions of resin and glass microballoon were processed and evaluated for tensile, flexural and compressive properties. The effect of nature and volume fraction of microballoon on the mechanical properties was studied. The mechanical properties showed a gradual decrease in strength with increase in volume fraction of microballoon. The specific strength values also manifested a similar order. A similar behaviour was observed for syntactic foams with microballoons of varying true density. The properties increased proportional to the strength of the microballoon in resin-rich systems implying a strong microballoon-resin interface, corroborated by Scanning Electron Microscopy studies. The compressive modulus showed a decreasing trend with enhanced microballoon loading.

Introduction

Syntactic foams are composite materials consisting of hollow microspheres that are dispersed in a resinous matrix. These microspheres are commonly made from inorganic materials such as glass and silica; and polymeric materials such as epoxy resin, unsaturated polyester resin, silicone resin, phenolics, polyvinylalchohol, polyvinyl chloride, polypropylene and polystyrene [1–7]. Syntactic thermoset foams have recently evoked a lot of attention as low-density composites for a wide range of applications [8]. The matrices of these materials are generally thermosetting polymers. Inclusion of hollow microspheres dispersed in the thermoset resinous matrix reduces the density of the syntactic foams, in a controlled manner. Improvements in foaming, production techniques and resulting properties of thermosetting foams have projected syntactic foams as the material of choice for general applications. These foams do not usually exhibit a melting range and can often be used at higher temperatures compared to thermoplastic foams. Unlike most other foams, syntactic foams are materials whose density before curing is the same as that after curing [8, 9]. Such predictability is advantageous in the manufacturing process in aerospace structure. They find wide application in aerospace and automotive industries where, reduction for energy conservation is one of the important factors [10]. Syntactic foams as core material find application in the construction of sandwich structures [3, 5, 7, 11–14] used in satellites and radomes [15].

An array of thermoset resins have been developed to handle moderate-to high temperatures and tough conditions with ease. Cyanate esters constitute a high temperature resin family traditionally associated with space applications, because of their good thermal stability, low dielectric constant and extremely low moisture uptake compared to other resins of their class. Cyanate ester is known for its built-in toughness, micro-crack resistance and ease of processing [16]. Cyanate esters cure via addition polymerisation to produce a heterocyclic ring referred to as a polycyanurate network [17]. This polycyanurate network is

B. John · C. P. R. Nair (✉) · K. A. Devi · K. N. Ninan
Propellants and Special Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum 695022, India
e-mail: cprnair@gmail.com

B. John
e-mail: bbnjohn@yahoo.com

K. A. Devi
e-mail: k_ambikadevi@vssc.gov.in

K. N. Ninan
e-mail: kn_ninan@vssc.gov.in

responsible for the excellent properties of resulting polymer [15]. The ring formation can occur thermally or in the presence of a transition metal catalyst such as copper, cobalt or zinc and an active hydrogen donor [17]. A large variety of commercial dicyanates are available, the most versatile among them being Bisphenol A dicyanate (BACY), which was used as matrix in the processed syntactic foams. The properties of cyanate ester coupled with the low density of microballoons in syntactic foams render them better candidates for strong low-density structures.

Syntactic foams of epoxy [1, 3, 9, 11, 12, 18–25] phenolic resin [26, 27] and polyurethane [28] have been reported. There are only a very few reported literature on syntactic foams of cyanate ester [15]. In this paper, we report the processing and properties of cyanate ester syntactic foams with two types of microballoons, which differ in their shell thickness. The shell thickness of microballoon is defined in terms of a parameter called radius ratio (η), which is represented in Eq. 1.

$$\eta = \frac{r_i}{r_o} \tag{1}$$

where r_i is the internal and r_o is the outer radius of the microballoon. Increase in η corresponds to a decrease in wall thickness, which leads to decrease in true particle density and strength of microballoon [29]. Thus, when the volume fractions of matrix and microballoon are kept constant, any change in mechanical properties of syntactic foams can be related to the change in η of microballoon only. The effect of microballoon volume fraction and its nature on the mechanical properties of cyanate ester syntactic foam has been studied in this work. The variations of specific properties are also examined. By normalizing mechanical properties against the density, it is believed that the results would be useful for guiding future design of syntactic foams based on specific properties. The failure mechanism in flexurally failed samples has been studied by SEM analysis.

Experimental

Materials

BACY (2,2-bis (4-cyanatophenyl) propane) with a melting point of 79 °C supplied by Lonza Ltd (Switzerland) was used as received. The density of the cured resin system is 1,200 kg/m^3. Zinc octate (Amruth industries, Mumbai, India) and nonyl phenol (Fluka) were used as catalyst and co-catalyst for the oligomerisation of BACY. Glass microballoons K-37 and K-25, supplied by 3 M Company, US were used as fillers. The glass microballoon particle size distribution and properties, as provided by the manufacturer are listed in Table 1.

Processing

BACY was oligomerised in presence of zinc octate and 4-nonyl phenol (3:40, by weight ratio) under thermal conditions. Oligomerised cyanate ester being very viscous, the required amount of resin was dissolved in acetone, for proper dispersion of microballoon. Then weighed quantity of microballoon was added and thoroughly mixed to get a uniform dispersion of it. Mixing was done gently to avoid breakage of microballoon. It was then compression moulded to the required thickness. The curing was done according to the following cure schedule: 100 °C (1/2 h), 125 °C (1/2 h), 150 °C (1/2 h), 200 °C (1 h) and 250 °C (2 h). Blocks of dimension $100 \times 100 \times 5$ mm^3 were processed for tensile and flexural test coupon preparation (CYA and CYC series). The dimension of blocks for compressive strength determination was $100 \times 100 \times 12$ mm^3 (CYB and CYD series). The first eight blocks (CYA1-CYB4) shown in Table 2 were made with K-37 and the remaining (CYC1-CYD5) with K-25.

Mechanical testing

Test specimens with dimensions conforming to ASTM D-3039 ($5 \times 13 \times 69$ mm^3), ASTM D-790 ($5 \times 13 \times 100$ mm^3), ASTM D-695 ($12 \times 12 \times 24$ mm^3) were cut respectively for tensile, flexural and compressive strength testing from the processed syntactic foams. The testing was done in a Universal Testing Machine Instron Model 4202 at a crosshead speed of 5 mm/min for tensile and 2 mm/min for both flexural and compressive strength measurement. No extensometer was used for tensile testing. The gauge length and span length in flexural testing was 25 mm and 80 mm respectively and the test was done in three-point bend configuration. Three specimens were tested under each type for tensile and flexural testing. For com-

Table 1 Particle size distribution and properties of microballoons

Microballoon type	Microballoon size distribution(μm, by volume)			Effective top size (μm)	Target fractional survival (%)	Average true particle density (kg/m^3)
	10th percentile	50th percentile	90th percentile			
K-25	25	55	90	105	90	250
K-37	20	45	80	85	90	370

Table 2 Composition and density of the syntactic foams

Microballoon type	Syntactic foam type	Cyanate ester	Microballoon	Void content	Density (kg/m^3)
		Volume percentage			
K-37	CYA1	34.7	64.5	0.8	665
	CYA2	22.3	72.2	5.5	535
	CYA3	17.5	81.5	1.0	513
	CYA4	12.3	86.7	1.0	469
	CYB1	33.1	65.6	1.3	640
	CYB2	21.3	69.2	9.5	512
	CYB3	15.8	77.0	7.2	475
	CYB4	11.3	85.2	3.5	450
K-25	CYC1	31.1	64.1	4.8	534
	CYC2	26.7	69.7	3.6	494
	CYC3	22.2	75.4	2.4	455
	CYC4	18.5	80.1	1.4	422
	CYC5	11.3	87.7	1.0	355
	CYD1	31.9	62.6	5.5	539
	CYD2	25.1	73.3	1.6	484
	CYD3	19.0	80.7	0.3	430
	CYD4	13.3	85.2	1.5	373
	CYD5	9.4	89.1	1.5	336

pressive strength determination five specimens were tested for each type.

Scanning electron microscopy

The failed samples were coated with a conducting layer of gold using a sputtering unit and were examined in a Philips XL-30 Scanning Electron Microscopy.

Results and discussion

Density profile and void content of the syntactic foams

The density and volume percentage details of the processed syntactic foams are given in Table 2. The syntactic foams showed a gradual decrease in density with increase in volume fraction of microballoon due to the incorporation of low-density filler. For the same volume percentage of microballoon, syntactic foams with microballoon K-37 showed higher density owing to its higher true density. During the mixing of the resin with microballoon, entrapment of air is inevitable leading to voids in syntactic foams as shown in SEM picture (Fig. 1a). Therefore, the observed density will be lower than the theoretical density. The voids may also occur due to non-uniform distribution of resin in the syntactic foam block as illustrated in SEM picture. (Fig. 1b). Sometimes, a film of resin may enclose cluster of microballoons, making it difficult for the resin to penetrate into such cluster and wet the microballoons.

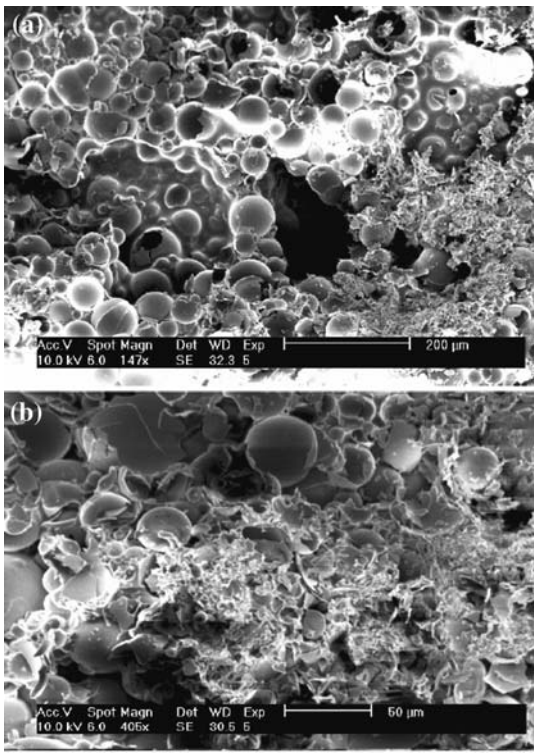

Fig. 1 (**a**) SEM picture showing voids in syntactic foam. (**b**) SEM picture showing non-uniform distribution of resin in syntactic foam

Theoretical predictions of the density could be made using the constituent weights and density and the rule of mixture relationship [9]. The void percentage has been calculated using the relation,

$$\text{Void percentage} = \frac{V - [W \times W_R/\rho_R + W \times W_M/\rho_M]}{V} \times 100 \quad (2)$$

where V and W are the volume and weight of foam block; W_R and W_M are the weight fractions of resin and microballoon; ρ_R and ρ_M are the densities of resin and microballoon respectively. The void-content in the present context refers to the space unoccupied by resin and microballoon. The maximum packing factor with spheres of same size is 0.74. However, the particle size distribution data reveals a wide range of distribution. As a result, the spaces created during the packing of large microballoons were occupied by smaller ones and the matrix. This can be visualized in the SEM picture (Fig. 2). Also the void percentage has been calculated assuming that the microballoons do not break during moulding. However, breaking of some microballoons takes place during compression moulding. This results in reduction of volume of the foam block, which in turn reduces the void percentage as per Eq. 2. All these account for the very low void percentage in the syntactic foams. Syntactic foams with void contents as low as 0.45% has been reported by Kartikeyan et al. [3, 4, 7]. With increase in microballoon content, normally we expect the void content to increase. However, in the case of K-25 syntactic foams, with increase in microballoon content the void percentage was found to decrease. This discrepancy can be explained as due to the partial oozing of resin and microballoon during compression moulding, in the case of resin-rich systems. It may be remarked that H. S. Kim et al. also observed the same phenomenon of reduction in void content with increase in microballoon volume percentage [30].

Mechanical properties

The variation of mechanical properties with volume percentage and shell thickness of microballoon can be understood from the plot of mechanical properties as a function of volume percentage of microballoon for the two types of microballoons, which will be discussed in the following sections. Since the mechanical properties of the syntactic foams depend also on the density of the foams (which in turn depends on the resin to microballoon ratio) as the density increases, strength increases [3].

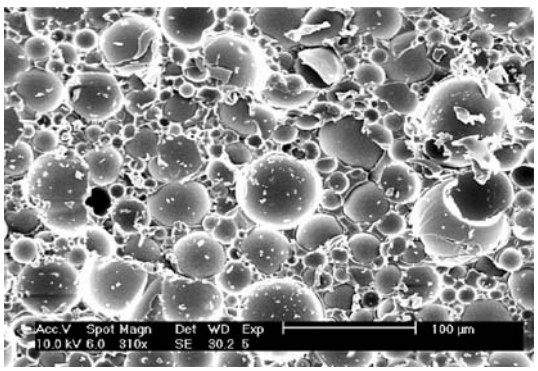

Fig. 2. SEM picture illustrating strong resin-microballoon interface and also the well packing of microballoons in the sample CYA4 (K-37)

Tensile strength

Figure 3a and b show the variations of tensile and specific tensile strength of cyanate ester syntactic foams as a function of volume percentage of microballoon, for the two different types of microballoons. The general trends in the tensile strength with increasing microballoon volume fractions are similar for syntactic foams with both types of microballoons. Syntactic foams with K-37 showed a higher value of tensile and specific tensile strength compared to those with K-25 except at higher volume fractions of microballoon. This shows the strong resin-microballoon interface and the likely failure through microballoon breaking as evidenced typically in SEM picture of the sample CYA4 in Fig. 2. Earlier studies have shown that for

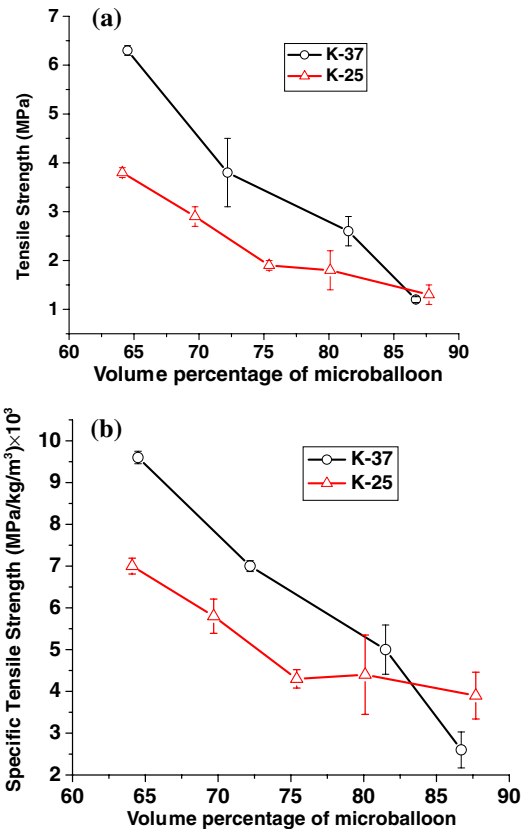

Fig. 3 (**a**) Variation of tensile strength with volume percentage of microballoon. (**b**) Variation of specific tensile strength with volume percentage of microballoon

microspheres of the same material composition, improved mechanical properties are obtained for microspheres with high density [8].

Inclusion of microballoon reduces the cyanate ester volume fraction, thereby reducing the tensile strength as a result of poor interfacial interaction between the matrix and the microballoon. The matrix serves as the load-bearing phase in the composite whereas microballoons only provide lightweight and minimal strengthening effect [8]. The reduction in the content of the load bearing resin outweighs the increase in stiff microballoons. Earlier studies have proved that a process involving resin fracture and resin-microballoon debonding, rather than crushing of microballoons dominated the tensile failure in syntactic foams [7]. At low volume fraction of filler, the failure occurs through microballoon breaking in the case of K-25 foams and matrix fracture in the case of K-37 foams. At high microballoon volume fractions (i.e., at low resin volume fractions) the failure occurs mainly due to resin-microballoon debonding and poor microballoon wetting, which makes the tensile strength values of both K-37 and K-25 syntactic foams, low and comparable. Interestingly, considering the low density of K-25 syntactic foams, specific tensile strength showed higher values for K-25 systems compared to the K-37 systems, at high volume fractions of microballoon.

Flexural strength

Flexural and specific flexural strength variations of the syntactic foams with microballoon volume fractions are depicted in Fig. 4a and b. Both flexural and specific flexural strength decreased with increase in volume percentage of microballoon for the two types of syntactic foams. With increase in microballoon volume fraction, the layer of matrix surrounding the microballoon becomes very thin. Therefore, the flexural strength decreases due to easy fracture of the thin film of matrix or resin to microballoon debonding. During flexural loading, the specimen is subjected to compression stresses on the top part and to tensile stresses at the lower part. It is known that if the microballoon strength is low enough and their fracture takes place during bending, then their inherent properties significantly affect the flexural properties of syntactic foams. If the microballoon strength is high and their fracture doesn't takes place in the syntactic foams, then the foam properties are governed by the properties of matrix material [31]. The high value for K-37 syntactic foams is attributed to the high strength of K-37 microballoons. Fewer microballoons are broken under the applied load in the case of K-37 syntactic foams as illustrated in the micrograph of the flexurally failed sample, CYA4 (Fig. 5a). On the other hand K-25 microballoons break more easily thereby

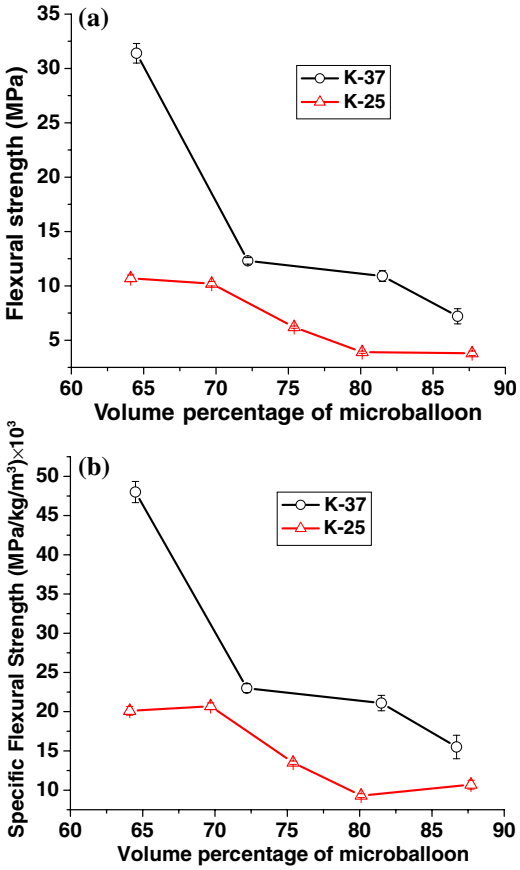

Fig. 4 (**a**) Dependency of flexural strength on volume percentage of microballoon. (**b**) Dependency of specific flexural strength on volume percentage of microballoon

reducing the strength of the material (Fig. 5b). Thus, in the present case, the inherent property of the microballoon has a say in the properties of the resultant composites. In both the samples CYA4 and CYC5, the volume percentages of microballoons (~87%), resin (~12%) and void (~1%) are almost same. In CYA4 based on K37, fewer microballoons are broken whereas in CYC5 with K25 almost all microballoons are broken, evoking the influence of shell thickness of microballoons on the flexural behaviour. This also implies that compressive part of the flexural load has more weightage than the tensile part. This shows a good resin-microballoon bonding and a combination of resin fracture and microballoon breaking in dictating the mechanical strength of the foam composites.

Flexural properties are also found to depend on the void content. The crack will initiate from an oversized void when the foam is subjected to flexural load. In the case of K-25 syntactic foams, there is only a marginal change in void content with increase in microballoon composition. Therefore in these cases, the variation of flexural strength is very marginal. But in the case of the sample CYA2 that has a void content of 5.5%, there is a steep decrease in

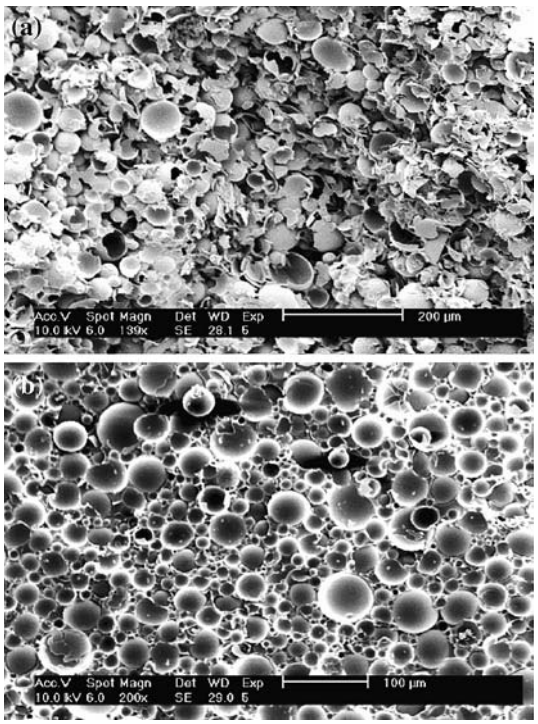

Fig. 5 (**a**) SEM picture of flexurally failed CYC5 (K-25) showing broken microballoons. (**b**) SEM picture of flexurally failed CYA4 (K-37) showing fewer microballoon breaking

flexural strength. This clearly points out the effect of void content on flexural strength.

Compressive strength

Figure 6a and b show the variation of compressive and specific compressive strength of syntactic foams with volume percentage of microballoons. Compressive strength and specific compressive strength showed a gradual decrease with increase in volume fraction of microballoon. Compressive strength depends on volume fraction of microballoon, void content and shell thickness of microballoon. When the resin content is high, the microballoons get smeared with the resin thus preventing the direct transfer of load to microballoon. For syntactic foams under compressive loading the matrix serves as the load-bearing phase. As the microballoon volume fraction increases, (and resin volume fraction diminishes) the microballoon takes up more loads under compression. But the load bearing capacity of microballoons is not well pronounced. Due to high volume fraction of microballoon, the layer of resin between microballoons is very thin and it tends to fracture easily under stress. Thus incorporation of microballoon decreases the compressive strength.

Effect of microballoon shell thickness on mechanical properties of syntactic foams has been studied in detail by

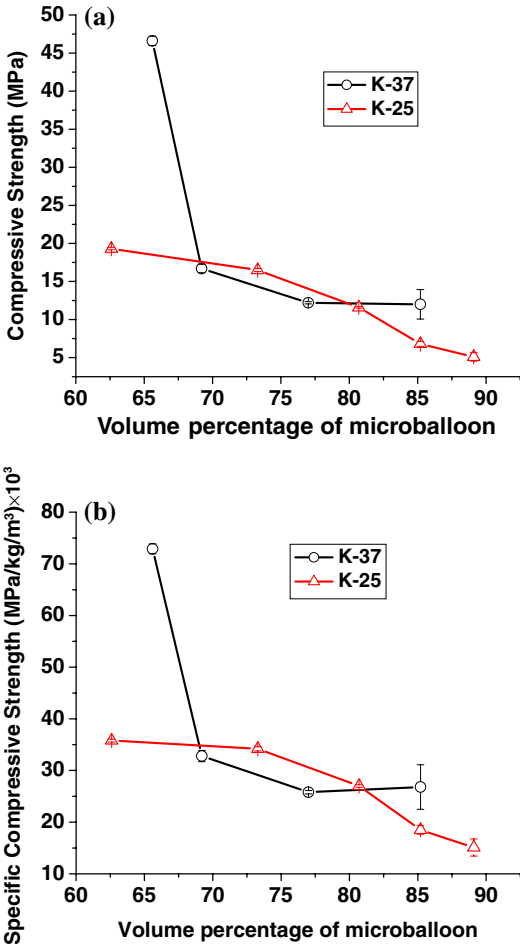

Fig. 6 (**a**) Variation of compressive strength with volume percentage of microballoon. (**b**) Variation of specific compressive strength with volume percentage of microballoon

Gupta et al. [6]. The variation of compressive strength with shell thickness can be associated with the different interaction of the microballoon to the externally applied stress. Comparing syntactic foams with K-25 and K-37, the latter showed a higher value of compressive strength due to its high wall thickness or low radius ratio, making K-37 microballoons less susceptible for breaking compared to K-25. Contrary to expectation, syntactic foams with K-37 showed lower compressive strength for microballoon volume percentages 69 and 77 (corresponding to samples CYB2 and CYB3). This can be attributed to the higher void content (9.5% and 7.2%) for these cases. Comparing CYB1 and CYB2, wherein the microballoon volume percentage is increased from 65.6% to 69.2%, there is a steep decrease in compressive strength (from 72.9 MPa to 32.8 MPa) as illustrated in Fig. 6a. This further substantiates the effect of void content on compressive strength. The effect of void content is also reflected in the compressive modulus values of the syntactic foams (Table 3). The high void content in CYB2 and CYB3 resulted in decreased compressive

Table 3 Compressive modulus values of the syntactic foams

Syntactic foam type	Compressive modulus (MPa)	Syntactic foam type	Compressive modulus (MPa)
CYB1	950	CYD1	620
CYB1	520	CYD2	600
CYB1	360	CYD3	400
CYB1	540	CYD4	360
		CYD5	210

modulus values for the two. The crack initiation could occur locally at the void and then propagate laterally through stress concentration on adjacent microballoons. Earlier studies also evoked the effect of void content on mechanical properties [1]. The corresponding specific strength values also followed the same trend.

The typical stress–strain curves for some of the syntactic foams under compressive loading are depicted in Fig. 7. The stress–strain curves of the syntactic foam under compressive loading has been studied by several researchers [6, 9, 8, 11, 23, 30]. The failure modes of the syntactic foams under compressive loading can be established from an observation of the stress–strain curve under compressive loading. All the curves showed a peak value for stress, which corresponds to the point of crack initiation. The region before the peak stress corresponds to the elastic deformation of the syntactic foams. After reaching the maximum, the stress value decreased and became nearly constant for further compression. This region is referred to as the plateau region or densification stage. The plateau region corresponds to energy absorption in the process of crushing of microballoons. At this stage the microspheres are crushed, exposing their internal hollow volume. Microsphere debris and matrix resin occupy the volume while getting compressed [6]. Interestingly, the plateau region is absent in the stress strain curve for CYB1, which shows that here, the failure takes place by fracture of matrix rather than microballoon. Thus for CYB1, which has high resin volume fraction, it is the resin that carries most of the load, whereas the high strength microballoons resists compression.

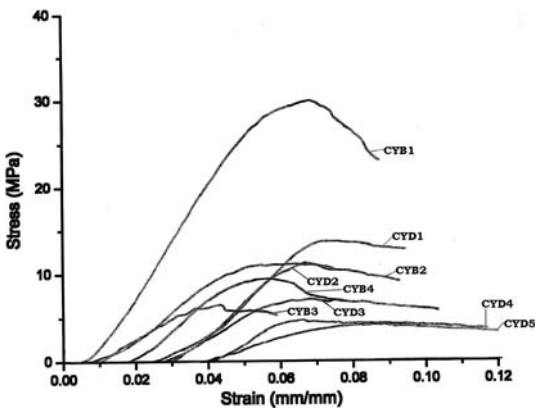

Fig. 7 Stress–strain curve for syntactic foams under compressive loading

The difference in fracture mechanism of the syntactic foams under compressive loading can be better explained from a macroscopic examination of the failed specimens. The specimens showed remarkable difference in failure modes with increase in microballoon volume fraction. The macroscopic feature of the syntactic foams failed under compressive loading is shown in figure (Fig. 8a–d). The samples CYB1, CYB2 and CYB3 showed a vertical cracking perpendicular to the direction of the applied load. Typical cracking pattern for CYB1 and CYB3 are indicated in Fig. 8a and b respectively. Since these syntactic foams were made with K-37 with higher shell thickness, it is obvious that the failure has taken place by fracture of resin. But, for CYB2 and CYB3 the stress–strain curve shows densification regions illustrating that for these two samples, resin fracture is also accompanied by crushing of microballoons. In the case of CYB4, the vertical cracking is not present but shows compression at the top and bottom. This is happened due to low resin content in this case. The microballoons have to withstand the applied load, thereby getting compressed. Here, the microballoons are broken uniformly throughout the specimen, dissipating the load and thereby resisting the catastrophic failure of the sample. For K-25 syntactic foams, macroscopic examination reveals that the fracture modes are more or less identical. Thus, in the case of K-25 syntactic foams, irrespective of whether the foam is resin rich or not, the failure takes place by a microballoon crushing mechanism. This is also evidenced in the stress–strain curve for K-25 syntactic foams, which showed densification region for very high strain rates.

Conclusions

Cyanate ester syntactic foams with varying densities were processed by varying the volume fraction of microballoon. The mechanical properties of syntactic foams depend on volume percentage of microballoon, density and shell thickness of microballoon. Incorporation of microballoon reduces the density as well as the mechanical properties. Microballoons with high density and wall thickness resulted in relatively increased mechanical properties unless certain structural defects such as voids affect it adversely. Specific mechanical properties also manifested similar order. The failure mechanism for tensile and flexural tests were comparable i.e., resin fracture, resin-microballoon debonding and cracking of microballoon. However,

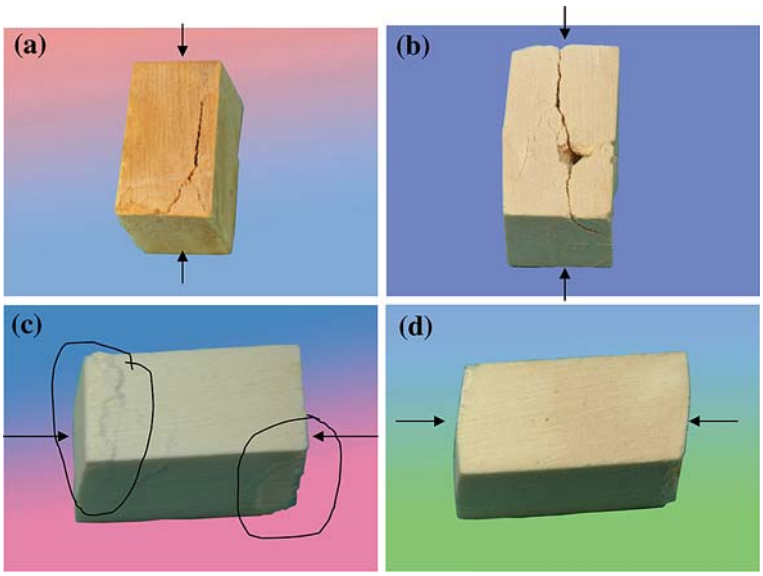

Fig. 8 Photograph of the syntactic foams failed under compressive loading. (**a**) and (**b**) shows vertical cracks in the samples, CYB1 and CYB3 respectively. (**c**) Small cracks at top and bottom in the case of CYB4 (shown in marked region). (**d**) Deformations at the top and bottom of the sample CYD3, no visible cracks are seen. (In all the cases the arrows point to the direction of applied load)

microballoon fracture and presence of void-content contributed mainly to the failure under compressive loading.

Acknowledgements The authors acknowledge Director, VSSC for granting permission to publish this paper. The assistance given by Ms. Sirisha (MCD) is acknowledged. Bibin John thanks Indian Space Research Organisation for a Fellowship.

References

1. Gupta N, Karthikeyan CS, Sankaran S, Kishore (1999) Mat Charact 43:271
2. Marur PR (2005) Mat Lett 59:1954
3. Karthikeyan CS, Sankaran S, Kishore (2004) Mat Lett 58:95
4. Karthikeyan CS, Sankaran S, Kumar MNJ, Kishore (2001) J Appl Poly Sci 81:405
5. Bardella L, Genna F (2001) Inter J Solids Struct 38:7235
6. Gupta N, Woldesenbet E, Mensah P (2004) Comp Part A Appl Sci Manufact 35:103
7. Karthikeyan CS, Sankaran S, Kishore (2005) Macro Mat Eng 290:60
8. Wouterson EM, Boey FYC, Hu X, Wong S-C (2005) Comp Sci Tech 65:1840
9. Bunn P, Mottram JT (1993) Composites 24:565
10. Sharma SC. In: Composite materials. Narosa Publishing House, New Delhi, p 19
11. Gupta N, Woldesenbet E (2003) Comp Struct 61:311
12. Kim HS, Oh HH (2000) J Appl Poly Sci 76:1324
13. Gupta N, Woldesenbet E (2002) In Proceedings of ETCE 2002 ASME engineering technology conference on energy. TX, Houston, February 2002
14. Bardella L, Genna F (2001) Inter J Solids Struct 38:307
15. Sankaran S, Ravishankar BN, Ravisekhar K, Kumar MNJ (2005) In: Proceedings of ISAMPE national conference on composites, INCOM-4. Amrita Vishwa Vidyapeetham, Coimbatore, India, Dec.2005
16. High Performance Composites, November 2004, p 24
17. Nair CPR, Gopalakrishnan C, Ninan KN (2001) Polym Polym Comp 9(8):531
18. Benderly D, Rezek Y, Zafran J, Gorni D (2004) Polym Comp 25(2):229
19. Song B, Chen W, Yanagita T, Frew DJ (2005) Comp Struct 67:289
20. Song B, Chen W, Yanagita T, Frew DJ (2005) Comp Struct 67:279
21. Kim HS, Khamis MA (2001) Comp Part A: Appl Sci Manufact. 32:1311
22. Kim HS, Mitchell C (2003) J Appl Polym Sci 89:2306
23. Gupta N, Kishore, Woldesenbet E, Sankaran S (2001) J Mat Sci 36:4485
24. Palumbo M, Tempesti E (2001) Appl Comp Mater 8:343
25. Kishore, Shankar R, Sankaran S (2005) Mat Sci Eng A 412:153
26. Huang Y-J, Vaikhanski L, Nutt SR (2006) Comp Part A Appl Sci Manufact 37:488
27. Vaikhanski L, Nutt SR (2003) Comp Part A: Appl Sci Manufact 34:1245
28. Rittel D (2005) Mat Lett 59:1845
29. Woldesenbet E, Gupta N, Jadhav A (2005) J Mat Sci 40:4009
30. Kim HS, Plubrai P (2004) Comp Part A Appl Sci Manufact 35:1009
31. Maharsia R, Gupta N, Jerro HD (2006) Mat Sci Eng A 417:249