2 Types of Syntactic Foams

The properties of syntactic foams are very much dependent on the nature of polymer matrix employed. Studies have therefore focused on exploring different polymer matrices for syntactic foams. Apart from the nature of the matrix, concentration of the matrix, type of curative, and type of microballoon are critical parameters in determining properties. This chapter focuses on syntactic foams based on various polymer systems.

2.1 Epoxy Syntactic Foams

Epoxy syntactic foams have been the most extensively studied because they can be formulated in various ways to give the desired end product. They are preferred to other matrix systems owing to their high strength and stiffness, thermal and environmental stability, creep resistance and lower shrinkage and water resistance [1]. The high viscosity of epoxy is a disadvantage, but the problem can be solved by adopting suitable processing techniques and by material selection [2–3]. Bisphenolic, novolac and other structural epoxy resins in combination with different microballoons have been used to process syntactic foams. Epoxy syntactic foams with polystyrene, carbon, phenolics (BJO-0930), glass and mineral microballoons have been reported [2, 4–5]. Epoxy syntactic foams have been widely used in sandwich composites. They have been used as a thermal protection system in rocket science, particularly to protect the substructures from the heat flux of the exhaust plumes.

The performance of epoxy syntactic foams is dependent upon volume percentage, shell thickness and the material of microballoons.
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The properties of epoxy syntactic foams can be further tuned by appropriate choice of the resin system, blending with other polymer resins, and by suitably selecting the curative. The properties are also found to depend upon the process technique followed, i.e., casting and moulding.

The effect of microballoon volume fraction on the properties of epoxy syntactic foams with microballoons of density 220, 320, 380, and 460 kg/m³ (designated SF22, SF32, SF38 and SF46, respectively), has been reported by Gupta and co-workers. These microballoons have identical size but different shell thickness. The tensile strength showed a decreasing trend when the microballoon volume percentage was increased from 30% to 60%. All types of syntactic foams showed a decrease in tensile strength of 60–80% compared with the neat resin. The specific strengths of SF22 and SF32 foams do not show variation with microballoon concentration in the range of 30–60 vol%. The values showed a decreasing trend for SF38 and SF46 foams, but these values are also closely spaced and the trend can be considered to be nearly constant. The modulus was found to increase with microballoon density [6].

Another study was conducted by Wouterson and co-workers for epoxy syntactic foams with three types of microballoons: 3M Scotchlite, K-15 and K-46 glass microballoons, and Phenoset BJO-093 hollow phenolic microballoons [7]. They showed that tensile and flexural strength decreased with increasing filler content, and was not affected by the component microspheres. The specific tensile strength showed a maximum value at 10 vol% microsphere, whereas specific flexural strength decreased with microballoon concentration for all types of microspheres used (Figure 2.1a and 2.1b). Tensile and flexural moduli showed different trends for each type of microsphere with increasing filler content [7].

The compressive properties of epoxy syntactic foams were reported by Bunn and co-workers. They studied the compressive properties of syntactic foams made from phenolic microballoons with different volume fractions. The bulk density of the foams varied from
Figure 2.1 Specific (a) tensile and (b) flexural properties of epoxy syntactic foam containing (■) K15, (▲) K46 and (●) phenolic microspheres. Reproduced with permission from E.M. Wouterson, F.Y.C. Boey, X. Hu and S-C. Wong, Composites Science and Technology, 2005, 65, 11–12, 1840. ©2005, Elsevier [7]
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1.5 g/cm³ to 0.78 g/cm³ when microballoon volume percentage was increased from 0% to 53%. A decrease in compressive strength was observed on increasing the microballoon volume fraction. The mean compressive yield strength ranged from 28 MPa to 71 MPa, and the mean initial tangent compressive modulus of elasticity ranged from 0.81 GPa to 2.7 GPa. Thus, the compressive yield strength and initial tangent modulus of elasticity were linearly dependent on the bulk density and the volume fraction of microballoons (Figure 2.2) [4]. Palumo and co-workers also observed a reduction in compressive strength from 70 MPa to 50 MPa as the weight percentage of the microballoons increased from 15% to 35% [8]. Zihlif and co-workers found that the density, elastic modulus, compressive yield stress and strain decreased with increase in the volume fraction of microballoons [9].

Studies by Wouterson and co-workers showed that the specific compressive yield strength decreased with increasing filler content for epoxy syntactic foams with phenolic and K15 microspheres. However, an upward trend is observed for syntactic foams with K46 microspheres. This is attributed to a relatively minor decrease in the compressive yield strength compared with the decrease in density. The difference in compressive strength of syntactic foams with K15 and K46 microspheres shows the influence of compressive strength on the wall thickness of microspheres. The specific compressive modulus increased with microballoon concentration for syntactic foams with K15 and K46, whereas in the case of phenolic microballoon syntactic foams, the modulus remained almost constant with microballoon concentration [7]. The compressive strength and modulus of epoxy syntactic foams was found to be higher for those processed using microballoons of higher shell thickness [7, 10–12]. The approach of changing the microballoon thickness while keeping the microballoon volume fraction constant is more effective than changing the microballoon volume fraction to change the syntactic foam density because it considerably increases the specific strength [11].

The moisture absorption of epoxy syntactic foams with S22 (microballoon density = 220 kg/m³) and K46 (microballoon density = 460 kg/m³) microballoons was found to be <1% at room temperature.
Figure 2.2 Variation of (a) compressive strength and (b) modulus with bulk density of epoxy syntactic foams. Reproduced with permission from P. Bunn and J.T. Mottram, *Composites*, 1993, 24, 7, 565. ©1993, Elsevier [4]
At 70 °C, S22-type syntactic foam absorbed 6.7% and 2.5% moisture in deionised and salt water, respectively, whereas K46 syntactic foam absorbed 3.9% and 1.9%, respectively, (Figure 2.3). A considerable decrease in modulus is observed in wet samples compared with dry samples of the same type. For S22-type syntactic foam, the decrease is 49%, 51%, 65% and 68%, respectively, for low-temperature deionised water, low-temperature salt water, high-temperature deionised water and high-temperature salt water. The corresponding decrease in the case of K46 syntactic foams was measured to be 48%, 64%, 57% and 60%, respectively. No significant difference was observed in the peak compressive strength of low-temperature specimens compared with the dry specimens. However, high-temperature specimens showed a decrease in compressive strength.

![Figure 2.3 Moisture absorption of epoxy syntactic foams at room temperature and 70 °C. Reproduced with permission from N. Gupta and E. Woldesenbet, Composite Structures, 2003, 61, 4, 311. ©2003, Elsevier [13]](image-url)
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of 36%, 33%, 34% and 31% for S22 deionised water-, S22 salt water-, K46 deionised water- and K46 salt water-immersed samples compared with the corresponding dry samples [13].

The fracture toughness of epoxy syntactic foams with glass microballoons of 220, 320, 380, and 460 kg/m³ density decreased from 2 MPa.m⁰.₅ to 0.6 MPa.m⁰.₅ as the volume percentage of microballoon increased from 30% to 65%. The decrease in fracture toughness was more (30%) as the volume percentage of the microballoons increased from 60% to 65% [14]. The fracture toughness of epoxy syntactic foams of lower microballoon concentrations, i.e., 0–20%, showed an increasing trend with increasing volume fraction of microballoons. This is attributed to crack front bowing mechanisms which assumes that microspheres can resist crack propagation and cause the crack front to bow out between the microspheres. High-density microballoons contribute to higher strength and stiffness in addition to crack bowing mechanisms due to the higher strength of the filler [15]. These two studies showed that there may be an optimum volume fraction of microballoons at which the fracture toughness reaches a maximum. Fracture toughness and fracture energy did not vary significantly with change in temperature in the range 50–125 °C [9].

The fracture toughness of epoxy (Epon 815) syntactic foams can be improved by changing the resin and curing agent without sacrificing mechanical and thermal properties. In syntactic foams in which epoxy was cured by anhydride (see Figure 2.4a and 2.4b), the addition of elastomer improved the fracture toughness whereas flexural strength was unaffected. For the cycloaliphatic amine-cured system (see Figure 2.4c), the addition of elastomer did not affect fracture toughness. The use of a cycloamine curing agent rather than a anhydride curing agent yielded an increase in fracture toughness of 30% due to better curing properties [16].

Dynamic mechanical analysis of epoxy syntactic foams shows a higher glass transition temperature (Tₐ) for the syntactic foams compared with the neat resin due to the reinforcing effect of the microballoons.
that affects the mobility of the polymeric chains in the interphase region between the matrix and the microballoons. The reduction in modulus values with increasing temperature is much lower in syntactic foams compared with neat resins. The room-temperature tan δ values of the syntactic foams showed a relatively large decrease compared with the neat resin due to the presence of rigid glass microballoons that was also at high concentration levels [17].

The coefficient of thermal expansion (CTE) of epoxy syntactic foams is lower than that of neat epoxy. The CTE of epoxy syntactic foam with carbon microspheres decreases as the filler concentration increases. The CTE values for foams with 0 (pure binder), 15, 20, and 25 vol% filler are $55 \times 10^{-6}$, $45 \times 10^{-6}$, $37 \times 10^{-6}$, and $13 \times 10^{-6} \degree C^{-1}$, respectively. These values do not change for temperatures up to 370 °C, which is important for materials used as thermal insulation where the heat loads can vary abruptly [18]. The dielectric constant was decreased with increase in frequency and filler content. Surface energy was higher compared with neat epoxy [19].
2.2 Phenolic Syntactic Foams

Phenolic resins have an important role as matrix in composite materials for thermo-structural and ablative applications. These excellent properties are due to the chemical structure, which primarily comprises C-C bonds in aromatic rings, which is a characteristic of phenolic groups. Under thermal stress, the phenolic structure slowly breaks up, releasing carbon. Syntactic foams based on phenolic resins are very advantageous because they can act as low-density ablatives. They have been successfully used for the thermal protection of atmospheric re-entry space vehicles and to prevent structures from the extreme heat flux of rocket exhaust plumes. They have the low thermal diffusivity and high char-forming properties desirable for good ablatives [20].

Phenolic syntactic foams and composites have become well-established in the offshore oil and gas industry over the past few years as highly fire-resistant, thermally insulative coatings and structures. Phenolic syntactic foams have good resistance to burning, and have improved thermal stability at 300 °C. The undesirable friable character of phenolic foams can be markedly improved by the introduction of microballoons [21]. Syntactic foams based on a phenolic binder (novolac) has a lower CTE (7 × 10^{-6} °C^{-1} for an apparent density of 200–300 kg/m³) compared with an epoxy-based system [18]. Phenolic syntactic foams based on silas microballoons, glass microballoons, IG-101 and K-37, amino microballoons, and fly ash have been reported [20–23].

Conventional condensate-cure phenolic resins are thermooxidatively fragile, so they were chemically modified to confer addition cure characteristics. One such polymer is propargyl ether novolac (PN) whose synthesis and structure are shown in Figure 2.5. The resin cures by an addition reaction of the propargyl group by a complex mechanism. The cured resin is stable up to 400 °C, unlike the condensate-cured one which starts losing weight at about 300 °C.

We studied the properties of phenolic syntactic foams and PN resin syntactic foams with K-37 microballoons. The composition of the syntactic foams is given in Table 2.1. The mechanical properties of phenolic syntactic foams with different microballoon concentrations
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Figure 2.5 Synthesis and curing of PN resin
(P1 to P5) and that of PN resin syntactic foam (PNM) is given in Table 2.2 [20].

Table 2.1 Composition and density of the phenolic syntactic foams

<table>
<thead>
<tr>
<th>Code for syntactic foams</th>
<th>Volume percentage</th>
<th>Density (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resin</td>
<td>Microballoon</td>
</tr>
<tr>
<td>P1</td>
<td>26.5</td>
<td>68.5</td>
</tr>
<tr>
<td>P2</td>
<td>22.3</td>
<td>72.1</td>
</tr>
<tr>
<td>P3</td>
<td>19.0</td>
<td>73.9</td>
</tr>
<tr>
<td>P4</td>
<td>16.8</td>
<td>76.0</td>
</tr>
<tr>
<td>P5</td>
<td>15.3</td>
<td>79.3</td>
</tr>
<tr>
<td>PNM</td>
<td>26.8</td>
<td>70.2</td>
</tr>
</tbody>
</table>


Though inferior to the properties of neat resin, tensile and flexural strength increased with volume fraction of microballoon and optimised at 72–74% by volume of microballoon. Both properties decreased with further addition of microballoon. The variation in tensile and flexural strength with microballoon volume fraction is due to the difference in interfacial bonding between microballoon and resin upon microballoon loading. The interfacial strength has been found to vary with microballoon volume fraction. When the resin content is high, smearing of the resin over microballoon occurs, making the interfacial strength excellent. Therefore, we expect tensile and flexural strength to decrease with increase in microballoon volume fraction. However, here the tensile and flexural strength were found to increase initially with increase in microballoon content. This has been ascribed to the inherent brittle nature of phenolic resin, which is reduced by adding microballoons at low volume percentages. Therefore, the microballoons act as a kind of reinforcing filler at
### Table 2.2 Mechanical properties of neat phenolic resin, phenolic syntactic foam, and PN resin syntactic foam

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Tensile strength (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Compressive strength (MPa)</th>
<th>Specific tensile strength (MPa/(kg/m$^3$)) $\times 10^{-3}$</th>
<th>Specific flexural strength (MPa/(kg/m$^3$)) $\times 10^{-3}$</th>
<th>Specific compressive strength (MPa/(kg/m$^3$)) $\times 10^{-3}$</th>
<th>Density (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat resin</td>
<td>20–70</td>
<td>50–105</td>
<td>70–210</td>
<td>18–58</td>
<td>40–88</td>
<td>58–175</td>
<td>1200</td>
</tr>
<tr>
<td>P1</td>
<td>8 ± 2</td>
<td>17 ± 2</td>
<td>35 ± 3</td>
<td>14 ± 4</td>
<td>30 ± 4</td>
<td>61 ± 5</td>
<td>570</td>
</tr>
<tr>
<td>P2</td>
<td>13 ± 3</td>
<td>24 ± 1</td>
<td>25 ± 2</td>
<td>24 ± 6</td>
<td>44 ± 2</td>
<td>46 ± 4</td>
<td>540</td>
</tr>
<tr>
<td>P3</td>
<td>14 ± 2</td>
<td>21 ± 1</td>
<td>19 ± 2</td>
<td>28 ± 4</td>
<td>42 ± 2</td>
<td>38 ± 4</td>
<td>504</td>
</tr>
<tr>
<td>P4</td>
<td>13 ± 1</td>
<td>18 ± 2</td>
<td>17 ± 3</td>
<td>27 ± 2</td>
<td>37 ± 4</td>
<td>35 ± 6</td>
<td>482</td>
</tr>
<tr>
<td>P5</td>
<td>9 ± 1</td>
<td>13 ± 1</td>
<td>14 ± 1</td>
<td>19 ± 2</td>
<td>28 ± 2</td>
<td>30 ± 2</td>
<td>467</td>
</tr>
<tr>
<td>PNM</td>
<td>6 ± 1</td>
<td>9 ± 1</td>
<td>12 ± 2</td>
<td>10 ± 2</td>
<td>16 ± 2</td>
<td>21 ± 3</td>
<td>581</td>
</tr>
</tbody>
</table>

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low loading levels. The decrease in tensile and flexural strength after attaining a maximum value has been ascribed to poor wetting of microballoons, which weakens the resin-microballoon interface. The syntactic foams failed easily at high volume fraction of microballoon due to easy debonding between microballoon and matrix, thereby reducing tensile and flexural strength [20].

Compressive strength showed a gradual decrease with increase in microballoon concentration. The compressive strength of three-phase syntactic foams primarily depends upon the properties of the microballoons, and the degree to which they can be packed into a volume, i.e., density and strength of the bond holding the microballoons. Neat phenolic resin has a compressive strength in the range 58–175 MPa. However, when microballoons are incorporated, the compressive strength decreases due to the easy crushing of microballoons. Thus, inclusion of microballoons interrupts the transfer of load in the matrix, thereby acting as weak points for the failure of the material [20].

From Table 2.2, it is obvious that the mechanical properties of PN resin syntactic foams are inferior to those of phenolic syntactic foam of comparable density. The void content is lower in PN resin syntactic foam than in phenolic syntactic foam of almost identical density. The higher void content in phenolic syntactic foam can be attributed to the inherent property of resole phenolic resin to form voids during curing due to the evolution of volatiles. Therefore, for syntactic foams containing the same material composition, PN resin syntactic foams exhibited marginally higher density than phenolic syntactic foams [20].

The specific mechanical properties of the syntactic foams, which are very important in comparing syntactic foams with different densities, are shown in Table 2.2. The specific mechanical properties followed the same trend as the corresponding mechanical properties. Although the inclusion of microballoons considerably decreased the mechanical properties, the specific properties of some of the syntactic foams were comparable with those of the neat resin. This highlights the applicability of phenolic syntactic foams for use in lightweight structural materials [20].
The dynamic mechanical properties of phenolic and PN resin syntactic foams were studied to assess their temperature capabilities. The typical dynamic mechanical analysis graphs of P1 and PNM in the temperature range 35–300 °C are shown in Figure 2.6(a) and 2.6(b), respectively. The storage modulus gradually decreased with increase in temperature for both syntactic foams. For PNM, the decrease in storage modulus with temperature is linear up to 300 °C whereas, for P1, there is a steep reduction in $E'$ in the temperature range.

![Figure 2.6](image-url) Variation of (a) storage modulus and (b) tanδ with temperature for P1 and PNM
160–210 °C. The stiffness values of the syntactic foams are dominated by the rigid glass microballoons, which do not undergo transition in this temperature range. Thus, the steep decrease in storage modulus for P1 in the temperature range 160–210 °C is a feature of phenolic resins (which are known to undergo softening in this temperature range). The maximum use temperature ($T_{\text{max}}$) of syntactic foams is taken as the temperature at which the storage modulus starts decreasing steeply in the thermograms. $T_{\text{max}}$ assessed this way was found to be 160 °C for P1. In the case of PNM, the modulus tends to continuously decrease (slowly) with temperature, unlike conventional phenolic resin. This implies weak bonding between the microballoon and resin, which relaxes the applied stress. The $\tan\delta$ profile shows a maximum at 200 °C for PI, in tune with the $T_g$ of the cured matrix. For the PN resin syntactic foam, the maximum occurs at 270 °C, close to the resin $T_g$. Analysis shows that $\tan\delta_{\text{max}}$ values of syntactic foams are lower than those of neat resin materials due to diminution in overall flexibility as a result of rigid fillers [20].

In the case of phenolic syntactic foams with IG-101 and silas microballoons, flexural strength, modulus and compressive strength decreased with increase in concentration of microballoon. Except for syntactic foams with silas microballoons, the properties are superior to those of phenolic foams [21]. For syntactic foams prepared from blends of six phenolic resins and carbon microbubbles, the compressive strength of the phenolic resin foam is equivalent to the strength of foams made from a polyimide resin [24]. The combined effect of good specific mechanical properties and the likely ablative characteristics make phenolic syntactic foams important lightweight material for aerospace applications.

Another class of addition cure phenolic resin that has also been explored for syntactic foams is polybenzoxazine. Benzoxazines have 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. These properties of the polybenzoxazine matrix render it a good candidate for syntactic foam composites. In general,
benzoxazines are synthesised from phenol, aniline and formaldehyde. The polymerisation of bisphenol-A based benzoxazine is shown in Figure 2.7. Here, the polymerisation occurs by the ring-opening polymerisation of the benzoxazine ring [25].

Our research group has studied the mechanical properties of polybenzoxazine syntactic foams with varying concentrations of K-37 microballoons. The variation of specific mechanical properties with microballoon concentration is depicted in Figure 2.8. Tensile and compressive properties were optimised at about 68% by volume of microballoon while flexural strength decreased marginally on increasing the microballoon content. Although the specific tensile and compressive strength showed a maximum followed by a decrease, the specific flexural strength systematically increased.

![Figure 2.7](image_url)

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2.3 Cyanate Ester Syntactic Foams

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 with other resins of their class. Cyanate ester is known for its built-in toughness, micro-crack resistance and ease of processing [26]. Therefore, syntactic foams derived from these resins will be a


with microballoon content. Polybenzoxazine is basically a phenolic resin, so these composites could be potential candidates for lightweight thermostructural applications, as in ablative thermal insulation [25].