CHAPTER 5

Foam Sandwich Composites with Cyanate Ester Based Syntactic Foam as Core and Carbon-Cyanate Ester as Skin: Processing and Properties

Foam sandwich composites were processed using cyanate ester-based syntactic foam as core and carbon fabric-cyanate ester composite as skin by a one-step compression moulding technique. The mechanical properties of the sandwich composites were evaluated in terms of flatwise tensile strength, flatwise compressive strength and edgewise compressive strength. The dependency of these properties on the core composition was investigated. The failure modes of the composites under different loading conditions have been examined.

A part of the results of this chapter has been published:
5.1 Introduction

Sandwich composites are widely used in marine, aerospace and other structural applications owing to their high stiffness and strength, and low specific gravity. Their areas of application include various types of transportation vehicles and packaging. They consist of two thin, but stiff skins attached to a lightweight core [Corigliano et al., 2000; Gupta and Woldesenbet, 2005]. The skins are usually made of glass- or carbon fabric-reinforced composites of a suitable resin. The core used in sandwich composites can be cellular foams, syntactic foams or other lightweight materials. Among the various foam materials, syntactic foams have an excellent combination of good compressive strength, low density, low radar detectability and low moisture absorption coefficient [Gupta et al., 2002]. In sandwich composites, the mechanical properties of syntactic foam-based cores are several orders of magnitude higher than those of the traditional foams [Hiel et al., 1993]. The closed cell structure has the advantage of continuous contact between the skin and the core, providing better interfacial strength compared to cellular foam cores used in sandwich constructions. Sandwich composites with different densities can be fabricated either by simply changing the volume percentage of resin and microballoon or by using microballoons of different shell thickness. These features make the syntactic foams better candidates as core materials for sandwich composites in aerospace and other structural applications [Woldesenbet et al., 2005].

Highly damage tolerant sandwich constructions can be obtained by using carbon fibre reinforced plastic (CFRP) as skins and a syntactic foam as core [Gupta and Woldesenbet, 2005]. CFRP skins, which are the structural backbones, provide high specific strength and stiffness to the sandwich. The syntactic foam core provides excellent shear tie between the skins. It supports the skin against buckling, localises the
impact damage and absorbs energy through a microballoon crushing mechanism [Hiel et al., 1993]. Though several resin systems have been attempted for forming the foam core, there are only very few reports on the use of cyanate ester for this purpose. This chapter presents the use of cyanate ester to constitute both the core and skin composites of the sandwich composites. Cyanate ester is known for its built-in toughness, micro-crack resistance and ease of processing. A major advantage of using cyanate ester as matrix is that there is no adhesive required for bonding the skin to the core due to the inherent adhesive property of the resin. They have higher $T_g$ in comparison to epoxy matrices. All these justify the use of cyanate ester-based syntactic foam as core in sandwich composites envisaged as lightweight structures for possible aerospace applications.

The mechanical properties of syntactic foams have been extensively studied by various researchers. Sandwich structures with syntactic foam as core have also been reported. Sankaran et al. have developed cyanate ester-based syntactic foam as core for E-glass sandwich composites for radome applications [Sankaran et al., 2005]. Gupta et al. have studied the effect of microballoon radius ratio and composition on the properties of sandwich composites [Gupta and Woldesenbet, 2005; Gupta et al., 2002; Woldesenbet et al., 2005; Gupta et al., 2002; Gupta et al., 1999]. They also reported the enhancement of energy absorption by way of nanoclay incorporation in syntactic foams for use as core of sandwich composites [Gupta and Maharsia, 2005]. Post impact damage and residual strength of syntactic foam-based sandwich composites have been studied by Hiel et al [Hiel et al., 1993]. Elastic design of syntactic foam-sandwiches has been reported by Bardella and Genna ["Bardella and Genna, 2001; Bardella and Genna, 2001]. Corigliano et al. have reported the experimental characterisation and numerical
simulation of sandwich composites with syntactic foam as core and glass fabric as skin [Corigliano et al., 2000].

This chapter concerns the processing of sandwich composites with cyanate ester-based syntactic foam as core and investigating the effect of syntactic foam core composition on the mechanical properties of the resultant sandwich composites. The external facings of the sandwich (skins) are made of carbon fabric / cyanate ester composites. Sandwich composites with different core compositions were processed. The mechanical performance of the sandwich composites has been evaluated in terms of flatwise tensile strength, flatwise compressive strength and edgewise compressive strength. The fracture features of the composites under different loading conditions have also been examined.

5.2 Experimental

5.2.1 Materials

The details of the materials used for the processing of the sandwich composites viz. 2, 2-bis (4-cyanatophenyl) propane (BACY), K-37 microballoon and carbon fabric are given in chapter 2.

5.2.2 Processing of the sandwich composites

BACY was oligomerised in presence of 4-nonyl phenol and zinc octate catalyst (40:3, by weight) under thermal conditions. Oligomerisation was done by heating BACY in presence of catalyst and co-catalyst at 90°C. Oligomerised cyanate ester was dissolved in acetone. Then, weighed quantity of microballoon was added to it and thoroughly mixed to get a uniform dispersion. Mixing was done gently to avoid breaking of microballoons. Acetone was then removed in a vacuum oven at 60°C.
Carbon fabric was impregnated with a solution of cyanate ester in acetone. It was then dried at room temperature for 18 hours. The prepreg composition was maintained at carbon fabric: cyanate ester = 60:40 (by weight). The prepregs were then cut into a square of 100mm size. The average thickness of each skin was 0.5 mm. The skin and cyanate ester-microballoon mixture were arranged in such a manner that the cyanate ester-microballoon mixture was placed in between two prepreg plies on both sides. It was then compression moulded to the required thickness. The curing was done according to the following cure schedule: 100°C (1/2hr), 125°C (1/2hr), 150°C (1/2hr), 200°C (1hr) and 250°C (2hr). The physical properties like density and volume fraction of the constituents were determined. The average thickness of the sandwich composites was 14 mm. Figure 5.1 shows photograph of the processed cyanate ester syntactic foam core sandwich composite.

**Figure 5.1** Photograph of the sandwich composite

### 5.2.3 Characterisation of the sandwich composites

The void content in the sandwich composites was calculated using the equation,

\[
\frac{(V_{SA} - V_{SK}) - [(W_{SA} - W_{SK}) \times W_R / \rho_R + (W_{SA} - W_{SK}) \times W_M / \rho_M] \times 100}{(V_{SA} - V_{SK})}
\]
where $V_{SA}$ and $W_{SA}$ are the volume and weight of sandwich block; $V_{SK}$ and $W_{SK}$ are the volume and weight of sandwich skin; $W_R$ and $W_M$ are the weight fractions of resin and microballoon; $\rho_R$ and $\rho_M$ are the densities of resin and microballoon respectively.

The mechanical properties of the sandwich composites viz. flatwise tensile strength, flatwise compressive strength and edgewise compressive strength were determined as per the test methods given in chapter 2.

5.3 Results and discussion

Table 5.1 gives the composition and physical characteristics of the processed foam sandwich composites. As the resin concentration in the foam core increases, the density of the sandwich composite increases. The void-content also increases with resin enrichment in the core. The void content in foam composites is an important factor affecting the mechanical properties. There are different possibilities for void formation in syntactic foams. In some cases where the microballoon concentration is very high, insufficient resin in between the microballoons leads to voids. Also, during the mechanical mixing of microballoon and resin, there is a possibility for entrapment of air. This entrapped air could act as voids in the foam structure. The void-content in the syntactic foam core is inevitable even after the application of vacuum to the resin-microballoon mixture as it is not possible to completely remove the entrapped air. In some other cases, a thin film of resin may surround a cluster of microballoon preventing penetration of resin into this cluster. At high resin volume percentage, the void-content was very high in the present study. This has been attributed to the partial oozing of resin and microballoon from the core during compression moulding. This point out the practical difficulty in the processing of syntactic foam sandwich composites with high resin-content by the one-step compression moulding method.
Table 5.1 The composition and density of the sandwich composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Core composition (in volume percentage)</th>
<th>Overall Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cyanate Ester</td>
<td>Microballoon</td>
</tr>
<tr>
<td>SA1</td>
<td>10.9</td>
<td>82.1</td>
</tr>
<tr>
<td>SA2</td>
<td>16.3</td>
<td>79.4</td>
</tr>
<tr>
<td>SA3</td>
<td>21.1</td>
<td>68.3</td>
</tr>
<tr>
<td>SA4</td>
<td>26.5</td>
<td>57.4</td>
</tr>
<tr>
<td>SA5</td>
<td>33.0</td>
<td>46.0</td>
</tr>
</tbody>
</table>

The void-content makes the syntactic foam core a three-phase system. The observed density of the sandwich composites was lower than the theoretical values calculated from the rule of mixtures due to the presence of voids. Sandwich composites based on syntactic foam as core with a void content up to 31% have been reported in literature [Papa et al., 2001]. Earlier studies on syntactic foams showed that presence of voids adversely affects the mechanical properties [Gupta et al., 1999]. The presence of voids decreased the flexural and compressive strength of cyanate ester syntactic foams as reported in chapter 4.

5.3.1 Mechanical properties of the sandwich composites

The mechanical properties of sandwich composites are greatly influenced by the properties of skin and core. The skin composition was fixed throughout the study (i.e. carbon fabric: cyanate ester = 60:40, by weight). The only change was in the composition of the core by varying the volume percentages of resin and microballoon. Since the properties of syntactic foams depend on the density which, in turn depends on volume percentages of microballoon and resin, these factors are also likely to determine
the properties of the resulting sandwich composites. Since these sandwich composites could find use as structural materials in aerospace applications, it is required that the mechanical properties of the sandwich composites be optimised by way of composition of the core. Hence, this aspect was examined in this study. A detailed investigation of the mechanical properties of the sandwich composites and their dependencies on the core composition form the subject of following sections.

5.3.1.1 Flatwise tensile strength

Flatwise tensile strength provides information on how well the facings are bonded to the core. It also reflects the flatwise tensile strength of the core, which is a critical factor in the design of sandwich structures. The test consists of subjecting the sandwich composite to a tensile load normal to the plane of the sandwich, such load being transmitted to the sandwich through thick loading blocks bonded to the sandwich facings. A proprietary adhesive developed by Adhesive section of VSSC, based on a modified urethane-epoxy adduct that cures at room temperature with an amine hardener, was used for bonding the specimens to aluminium blocks for flatwise tensile testing. The flatwise tensile bond test configuration is schematically shown in Figure 2.1 (a).

In the case of syntactic foam-based sandwich composites, the strength of the core as well as the interfacial strength between skin and core are of great importance in determining the flatwise tensile strength. The flatwise tensile strength, specific flatwise tensile strength (ratio of flatwise tensile strength to density) and failure modes of the sandwich composites are given in Table 5.2. The flatwise tensile strength (FTS) of the sandwich composites increased with increase in concentration of resin in the core. However, the FTS showed a diminishing trend on enhancing the resin-content beyond 26.5%.
Table 5.2 Flatwise tensile properties and failure mode of the sandwich composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Flatwise tensile strength (MPa)</th>
<th>Specific flatwise tensile strength (MPa/kg/m³) x 10³</th>
<th>Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1</td>
<td>1.4 ± 0.3</td>
<td>2.5 ± 0.5</td>
<td>Core failure</td>
</tr>
<tr>
<td>SA2</td>
<td>3.0 ± 0.3</td>
<td>4.9 ± 0.5</td>
<td>Skin- core debonding</td>
</tr>
<tr>
<td>SA3</td>
<td>3.8 ± 0.2</td>
<td>6.0 ± 0.3</td>
<td>Skin- core debonding</td>
</tr>
<tr>
<td>SA4</td>
<td>4.2 ± 0.2</td>
<td>6.6 ± 0.3</td>
<td>Skin- core debonding</td>
</tr>
<tr>
<td>SA5</td>
<td>2.2 ± 0.2</td>
<td>3.2 ± 0.3</td>
<td>Skin- core debonding</td>
</tr>
</tbody>
</table>

Two types of failure modes were observed when the sandwich composites were subjected to flatwise tensile loading. The failure mode was found to be core failure in the case of SA1 having the lowest resin-content. The low resin concentration in SA1 caused the resin-to-microballoon bonding weaker than skin-to-core bonding. Therefore, the failure of core took place in preference to skin-core debonding when a tensile load is applied normal to the plane of the sandwich. Skin-core debonding has been the failure mode in the rest of the cases. Here, the high resin-content makes the resin-to-microballoon bonding stronger than skin-to-core bonding. Figure 5.2 (a) shows the core failure in the case of SA1 and Figure 5.2 (b) shows the skin-core debonding in the case of SA-3. The low value of flatwise tensile strength for SA5 is attributed to the high void-content of the core. The high void-content has resulted in a reduction in area of contact between the skin and the core at the skin-core interface. As a result, the skin is peeled off easier from the core. The specific flatwise tensile strength values also manifested a similar trend.

Typical stress-strain curves for SA-1 and SA-5 tested under flatwise tensile loading are shown in Figure 5.3 (a) and 5.3 (b) respectively. Though the failure modes
in both cases were different, the nature of stress-strain curve is similar. In both cases, the point up to A corresponds to the region of elastic deformation. The point A refers to the point of core failure and skin-to-core debonding in SA-1 and SA-5 respectively. The systematic increase in the flatwise tensile strength of the sandwich composites upto SA-4 implies a stronger interfacial bond with increase in resin content of the core.

Figure 5.2 Sandwich composites failed under flatwise-tensile load. (a) Failure of core in the case of SA1. (b) Skin-to-core debonding in the sample SA3
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Strain (mm/mm)

(a)

3.0
2.5
2.0
1.5
1.0
0.5
0.0

Strain (mm/mm)

(b)

Figure 5.3 Typical stress-strain curve of (a) SA-1 and (b) SA-5 on flatwise-tensile loading

5.3.1.2 Flatwise compressive strength

The flatwise compressive properties of the sandwich composites were determined using the test method given in Section 2.2.5.6. It was observed that large amounts of debris are generated in compressive fracture, whereas tensile fracture shows only a small amount of broken pieces on the fracture surface. When a syntactic foam core-based sandwich is subjected to compressive loading, the microballoon breakage is the prominent failure phenomenon. The contribution of skin in load bearing is negligible in this case. The flatwise compressive properties of the sandwich composites are given in Table 5.3. The flatwise compressive strength values are found to increase with increase in resin concentration in the core. This is due to the better loading bearing property of the resin compared to that of the low strength microballoons. The flatwise compressive strength was not affected by the high void-content as in the case of SA5. This shows that the load withstanding ability of resin overcomes the likely adverse
effect of high void content in this case. The corresponding specific strength values also followed the same trend. The flatwise compressive modulus and the corresponding specific modulus values increased with increase in resin concentration. However, the high void content in the case of sample SA5 caused a slight diminution in the modulus.

Table 5.3 Flatwise compressive strength and modulus of the sandwich composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Ultimate Flatwise compressive strength (MPa)</th>
<th>Flatwise compressive modulus (MPa)</th>
<th>Specific Flatwise compressive strength $(\text{MPa}/\text{kg/m}^3) \times 10^3$</th>
<th>Specific Flatwise compressive strength $(\text{MPa}/\text{kg/m}^3) \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1</td>
<td>16 ± 2</td>
<td>155 ± 3</td>
<td>28 ± 4</td>
<td>276 ± 5</td>
</tr>
<tr>
<td>SA2</td>
<td>19 ± 1</td>
<td>181 ± 2</td>
<td>33 ± 2</td>
<td>297 ± 4</td>
</tr>
<tr>
<td>SA3</td>
<td>21 ± 1</td>
<td>182 ± 1</td>
<td>33 ± 2</td>
<td>289 ± 2</td>
</tr>
<tr>
<td>SA4</td>
<td>27 ± 1</td>
<td>381 ± 1</td>
<td>42 ± 2</td>
<td>595 ± 2</td>
</tr>
<tr>
<td>SA5</td>
<td>42 ± 5</td>
<td>374 ± 2</td>
<td>62 ± 7</td>
<td>550 ± 4</td>
</tr>
</tbody>
</table>

In order to explain the various failure features, the photographs of the sandwich samples subjected to flatwise compressive testing have been presented in Figure 5.4. During flatwise compression, it is the material at the central part of the sandwich that is likely to carry more load, due to stress concentration from both sides. In SA1 (where the microballoon volume percentage is high) when a compressive load is applied, the microballoons absorb the energy through uniform breaking. Therefore, no visible cracks were seen in the tested sample [Figure 5.4 (a)]. In the case of SA3, which is having higher resin-content than SA1, the stresses from both sides concentrate on the central part generating a horizontal crack on the sandwich core [Figure 5.4 (b)]. In the case of SA5, (with the highest void content) when a compressive load is applied, the voids tend to close and as a result no outburst of the core is observed [Figure 5.4 (c)].
The nature of the stress-strain curves for the sandwich composites under flatwise compressive loading was found to be the same in all the cases. The typical stress-strain curves for SA-2 are depicted in Figure 5.5. The stress values initially increases linearly
with strain, attains a maximum and then becomes almost constant. The maximum stress value in the curve is taken as the ultimate flatwise compressive strength. The region up to the peak stress corresponds to the elastic deformation regime of the syntactic foams. The slope of initial linear portion of the stress-strain curve is taken as the modulus of the composites. Though the maximum stress value for the sandwich composites is shown by SA-5 under flatwise compression, it is attained at a high percentage of strain, due to the uniform closing of voids in addition to the crushing of microballoons. This leads to a reduction in slope of the stress-strain curve for SA-5, thereby causing a slight decrease in modulus value.

![Stress-strain curve](image)

**Figure 5.5 Typical stress-strain curves for SA2 under flatwise compressive loading**

The flatwise compressive strength values reported in the present study (Table 5.3) are higher than those reported for sandwich composites composed of epoxy resin based syntactic foam core (average value=20 MPa) with a core density of 550 kg/m³.
[Corigliano et al., 2000; Papa et al., 2001]. However, the modulus values are lower in the present case.

5.3.1.3 Edgewise compressive strength

Edgewise compressive strength involves the determination of compressive strength of sandwich constructions in a direction parallel to the sandwich-facing plane. The details of the testing are given in Section 2.2.5.5. The edgewise compressive strength and modulus values of the sandwich composites are given in Table 5.4. The edgewise compressive strength increased with increase in concentration of cyanate ester in the core. There is not much increase in the strength value for SAS due to high void-content. The edgewise compressive strength values are lower than flatwise compressive strength but the modulus values for edgewise compression are comparatively higher. This is due to the fact that unlike in the case of flatwise compressive testing, during edgewise compressive testing a good proportion of the load is carried by the edges of the skin. When the stress increases, the microballoons in these two edge faces undergo crushing and the load is transferred to the skin. The tensile component of the compressive forces in the lateral direction causes the skin to bulge outwards. Therefore, further application of load results in the peeling of skin from the core. After the peeling of skin, the failure of core is initiated by a crack parallel to the plane of the skin as shown in Figure 5.6. Thus, the failure mode in the case of edgewise compressive testing is through peeling of skin from the core followed by failure of the core.

In the case of compressive loading on bare syntactic foams, the compression takes place in a slow manner with the breaking of microballoons. Even at the high microballoon volume fraction, the syntactic foams are not completely broken. But in the case of sandwich structures with high microballoon content, during edgewise
compression, the syntactic foam based core is completely destroyed. This is due to the sudden transfer of load to the syntactic foam core as the skin gives way.

Table 5.4 Edgewise compressive strength and modulus of the sandwich composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Edgewise compressive strength (MPa)</th>
<th>Edgewise compressive modulus (MPa)</th>
<th>Specific edgewise compressive strength (MPa/kg/m³) × 10³</th>
<th>Specific edgewise compressive modulus (MPa/kg/m³) × 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1</td>
<td>12.5 ± 0.5</td>
<td>620 ± 15</td>
<td>22.3 ± 0.9</td>
<td>1100 ± 25</td>
</tr>
<tr>
<td>SA2</td>
<td>14.8 ± 0.5</td>
<td>640 ± 20</td>
<td>24.2 ± 0.8</td>
<td>1050 ± 30</td>
</tr>
<tr>
<td>SA3</td>
<td>17.8 ± 0.5</td>
<td>720 ± 20</td>
<td>28.3 ± 0.8</td>
<td>1140 ± 30</td>
</tr>
<tr>
<td>SA4</td>
<td>19.0 ± 0.4</td>
<td>750 ± 40</td>
<td>29.7 ± 0.6</td>
<td>1170 ± 60</td>
</tr>
<tr>
<td>SA5</td>
<td>19.4 ± 0.4</td>
<td>540 ± 10</td>
<td>28.5 ± 0.6</td>
<td>790 ± 15</td>
</tr>
</tbody>
</table>

Figure 5.6 Photograph of sandwich composite failed under edgewise compressive loading

Previous reports show that the nature of the reinforcement that forms the skin plays an important role in edgewise compressive properties of the sandwich composites [¹Gupta et al., 1999]. Woldeabsnet et al. reported that the failure during edgewise compression occurs by the breaking of skin, followed by failure of core for sandwich composites with E-glass skin [²Woldeabsnet et al., 2005]. In the present case, the skin-
to-core binding strength is inferior to the longitudinal compressive strength of the skin composite material.

The stress–strain curve for the sandwich composites under edgewise compression can be related to visual observation for drawing conclusions regarding the failure modes. Figure 5.7 (a) and 5.7 (b) show the stress–strain curve for SA-1 and SA-3 respectively, which exhibited different failure features.

![Stress-strain curve for sandwich composites](image)

**Figure 5.7** Typical stress-strain curve for the sandwich composites under edgewise-compressive loading (a) SA-1 and (b) SA-3

In the case of both SA-1 and SA-3, the region from A to B refers to the elastic deformation of the sample. From B, the slow delamination of the skin from the core takes place for SA-1. This continues up to C. At C, the skin is fully delaminated and the load is suddenly transferred to the core. In the case of SA-1, since the resin content is very low, the sudden transfer of load results in catastrophic failure of the core. Whereas in SA-3, after the delamination of the skin, the stress-strain profile is akin to that of a high resin content syntactic foam under compression. In other words, the stress-strain
curve after the delamination of skin can be compared to that of syntactic foams under compression. After the delamination of the skin the stress starts increasing, becomes maximum and then decreases before becoming almost constant due to the densification of the microballoons. This is the stage where microballoons are crushed exposing their internal hollow volume. The maximum stress value in the curve is taken as the ultimate edgewise compressive strength of the sandwich composites. The edgewise compressive modulus and the corresponding specific modulus increase with resin content, but exhibits lower value for the highest resin-containing system (SA-5), due to the presence of high void-content.

5.4 Conclusions

Sandwich composites with cyanate ester syntactic foam as core could be processed by a one-step compression moulding method. Sandwich composites with different core compositions and property profiles are realisable by varying the volume percentage of microballoon in the core. A good skin-to-core adhesion could be achieved due to the inherent adhesive property of cyanate ester. Moderate resin-content is better in yielding low void-content core.

The composition of the foam core influences the flatwise tensile strength, flatwise compressive strength and edgewise compressive strength of the sandwich composites. Flatwise tensile strength increases with increase in resin-content of the core. However, the presence of voids at high resin concentration reverses the trend. The failure mode in the case of flatwise tensile loading changes from core failure in the case of low resin content system (SA-1) to skin-to-core debonding in the case of high resin-content systems (SA-2 to SA-5). The flatwise compressive strength and edgewise compressive strength and the corresponding modulus values increase with resin-content
of the core and are not much affected by the presence of voids at high resin loading. The failure mode under edgewise compression occurs by skin delamination followed by core crushing. Although, the flatwise compressive modulus and edgewise compressive modulus of the sandwich composites increase with resin-content, higher resin-content is detrimental for these properties. Depending on the application and strength requirement, the suitable composition of core can be selected.