Effect of Composition on Impact and Flexural Properties of Hybrid Glass Microballoons/Fly Ash Cenosphere Filled Vinyl Ester Matrix Syntactic Foams

Amol N. Patil, Pravin R. Kubade, Hrushikesh B. Kulkarni

Abstract: Syntactic foams are porous particulate composites fabricated by mixing hollow particles called micro-balloons into a matrix material such as metal, polymer, ceramic etc. Fillers i.e. micro balloons are used to decrease the amount of expensive matrix material and/or to enhance or tailor some properties of matrix materials. The different variations in density and properties of syntactic foam could be obtained by changing the material, volume fraction and/or density of micro balloons. Here the hybrid syntactic foams were synthesized by adding two different filler materials that are hollow glass microballoons and flyash cenospheres into vinyl ester matrix. Two types of hybrid systems are created one with 50% total filler content and another with 60% total filler content in a matrix whereas, within these hybrid systems an internal composition of two fillers were varied in a step of 25 vol% with respect to each other. Hybridization of two different types of ceramic microballoons in vinyl ester matrix gives maximum 111% increase in impact strength with respect to plane hollow glass microsphere syntactic foam. Hybridization also causes increase in flexural strength and Flexural modulus by 39% and 58% respectively.

Keywords: Syntactic Foam, Polymer Matrix, Glass Microballoons, Flyash Cenospheres, Impact Strength, Flexural Strength, Flexural Modulus

I. INTRODUCTION

Syntactic Foams were buoyant materials generally used for deep-sea applications and introduced back in the 1960s. Currently, syntactic foams are used in aerospace applications, airplane and ship structures. Syntactic foams are porous particulate composites fabricated by mixing hollow particles called micro-balloons into a matrix material such as metal, polymer, ceramic etc. Hollow fillers i.e. micro balloons are mixed in matrix decreases the amount of expensive matrix material and also add up some different properties to matrix materials. [1] Typical examples of microballoons are hollow glass microspheres, flyash cenospheres, polymeric microballoons, carbon microballoons, metal oxides, etc. Syntactic foams are familiar for their high specific compressive strength, less moisture absorption and better damping characteristics, higher thermal and chemical stability, high damage tolerance. [2] On account of these properties syntactic foams are used as core material for sandwich composites. Thermal insulation and conduction, weight-susceptive structures, sports equipment’s, body armor, etc. are some applications where syntactic foams are used as core material. Along with static and dynamic forces; the sandwich core also may get subjected to the impact as well as bending forces during their service life. Therefore they must be capable to withstand impact and flexural load along with static and dynamic loads. Increased interest of transportation sector in the lightweight composites has built considerable interest in syntactic foams; therefore, analyzing the impact and flexural performance of syntactic foams and linking it to assorted material constraint is important for their various applications [3].

Literature on syntactic foam highlights the present status of different polymer matrix materials, filler materials, micro-scale and nano-scale reinforcement, their manufacturing/processing method and their effects on the properties of syntactic foams with deformation and fracture mechanics. Nano scale reinforcement such as addition of carbon nano-fiber into syntactic foam has significant improvement in flexural strength and fracture toughness. Flexural strength and fracture toughness improved considerably with addition of CNFs up to 1.5 vol. % in hollow carbon microspheres phenolic resin syntactic foam [4]. Some studies show that modification of hollow carbon microspheres with glutaric-dialdehyde coupling agent facilitated better matrix-to-microsphere adhesive strength [5]. Nano-clay reinforcement also increases the tensile properties, flexural strength, toughness and compressive properties of hollow glass filled syntactic with addition of 2 vol.% and 4 vol.% [6]. Flyash cenosphere vinyl ester matrix syntactic foam showed an improvement in flexural modulus with comparison to matrix resin [1]. Studies shows that the absorbed impact energy decreases inversely to vol% of glass microballoons in vinyl ester matrix syntactic foam and raises with an increase in wall thickness of glass microballoons [7]. Ferreira et al. showed a reduction in impact energy with an increase in volume percentage of fillers. They also reported that glass fiber reinforced syntactic foam absorbs more impact energy than carbon fiber at a 45 vol% [3].
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Izod impact strength increases by mixing of 10 wt.% of phenolic microballoons in vinyl ester. [8] Studies show that the increment in reinforcement for syntactic foam causes to improve the flexural, compression, impact and tensile properties of the syntactic foam [9,10]. Mechanical Properties of polymer matrix can be improved by addition of filler [31-36]. However, there are a very few researchers who attempted to hybrid two different material microballoons at time. In present work, hybrid syntactic foam is synthesized by using two different fillers (i.e. glass microballoons and flyash cenospheres) into a vinyl ester matrix. The primary filler ‘hollow glass microspheres’ are highly engineered materials made up of soda-lime-borosilicate glass and possess good properties such as good specific strength, uniformity of their surface, resistivity to wetting, low viscosity of the resin-microballoons mixture, less cost and simplicity of production [11]. The secondary filler ‘flyash cenospheres’ are a waste by product extracted from flyash. Flyash cenospheres generally consist of empty circles of silica and alumina and possess characteristics such as good specific strength, irregularity of their surface, average-wetting resistivity, good energy absorption properties. Flyash cenospheres provides good alternative to replace conventional fillers at very low cost and thereby decreases cost of composite and also reduces land pollution [12]. The hybrid syntactic foam fabricated from these two ceramic microballoons with dissimilar properties and surface characteristics studied in present work for various loading conditions such as impact and flexural. The effect of variation in glass microballoons and flyash cenospheres composition on the impact and flexural properties of hybrid syntactic foam is investigated using Izod impact test and three point bending test method respectively.

II. MATERIAL AND METHODS

A. Materials

Vinyl Ester resin with 45% of styrene content is used as matrix material. Vinyl ester resin used in present work is synthesized from bisphenol-A diglycidyl ether (DGEBA) and poses density of 1.23 g/cm3. A dilute solution of Methyl ethyl ketone peroxide (MEKP) with density of 1.065 g/cm3 was used as a hardener. Hardener and vinyl ester resin was supplied by S.S. Enterprises, Pune, India. Glass micro balloons trade named as K20 from 3M India was used as primary fillers. Flyash cenospheres from Petra Buildcare Products Pvt. Ltd. Mumbai. K20 Glass micro-balloons are used as primary fillers. Flyash cenospheres from Petra Buildcare Products Pvt. Ltd. Bhavnagar are used as secondary fillers. Some typical properties of glass microballoons and flyash cenospheres are presented in Table 1 and Table 2, respectively.

Table- I: Properties of glass microballoons (Manufacturer data)

<table>
<thead>
<tr>
<th>Microballoon types</th>
<th>Density (g/cm³)</th>
<th>Particle size (μm) Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>True</td>
<td>10⁰th %</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>True</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Fabrication of Hybrid Syntactic Foams

Fabrication technique for hybrid syntactic foams is limited to hand layup method to avoid the breakage of microballoons during fabrication. The vinyl ester resin with MEKP hardener is used as matrix. Resin to curing agent (Hardener) ratio was kept at 97:3 as described by the supplier. The weighted quantity of mixture of glass micro balloons and flyash cenospheres fillers is added to resin to form slurry. The slurry is then transferred into an aluminum mold of required dimensions of test specimens. Mold was kept at room temperature for curing for about 20 hrs. These molds are then placed in oven for then 3 h at 72°C for post curing.

Table- II: Properties of flyash cenospheres (Manufacturer data)

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Chemical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>True particle density</td>
<td>0.6 – 0.8 gm./cc</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.25 – 0.45 gm./cc</td>
</tr>
<tr>
<td>Hardness (MOH)</td>
<td>5 - 7</td>
</tr>
<tr>
<td>Particle size</td>
<td>Less than 300 Microns</td>
</tr>
<tr>
<td>Crush strength</td>
<td>10-20.68 MPa</td>
</tr>
<tr>
<td>Packing factor</td>
<td>60-65%</td>
</tr>
<tr>
<td>Melting point</td>
<td>1500 oC</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt; 0.8 %</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2 % max.</td>
</tr>
<tr>
<td>Sinkers</td>
<td>&lt; 5 %</td>
</tr>
<tr>
<td>Oil absorption</td>
<td>16 – 18 g/100g</td>
</tr>
</tbody>
</table>

C. Design of experiments and Specimen Coding:

Two types of hybrid systems are created one with 50% total filler content and another with 60% total filler content in a matrix, i.e. the matrix to filler ratio kept for first experiment is 50:50 and for second experiment the matrix to filler ratio is 40:60, whereas an internal composition of two fillers was varied in a step of 25 vol% with respect to each other.
The following specimen coding is used as XXHSF-YYY-ZZZ. HSF is an abbreviation of hybrid syntactic foam whereas XX represents total vol% of mixture of two fillers. The abbreviation YYY represents K20 Hollow glass microballoons with volume fraction and ZZZ represents the volume fraction flyash cenospheres, respectively in total filler volume fractions fillers.
For example, 60HSF-75-25 represents hybrid syntactic foam with 75 vol% of K20 glass microballoons and 25 vol% of flyash cenospheres in total filler volume fraction of 60.

### III. TEST METHODS

ASTM D256-02 standard was used to perform Izod impact test on hybrid syntactic foam specimens [13]. The specimens with dimensions of 55*10*10 (l*b*t) were prepared as recommended in standard. ASTM D 790-03 standard was used to perform the flexural test. Test was carried out on a universal testing machine with three-point bending configuration. Specimens with dimensions of 127*12*3.2 (L*W*T) mm3 was prepared and tested for 52 mm span length in order to keep span to depth ratio equal to 16:1 as specified in standard [14]. The surface morphology of fractured hybrid syntactic foams was examined by TESCAN VEGA 3 tungsten thermionic emission-scanning electron microscope with operating voltage of 10 KV.

### IV. RESULTS AND DISCUSSION

#### A. Density and porosity

The theoretical density of hybrid syntactic foam is calculated by using the following rule

\[
\rho_{ct} = \left(V_m \cdot \rho_m\right) + \left(V_r \cdot \rho_f\right) \quad …… (1)
\]

Here, V and \( \rho \) signify the volume percentage and density, correspondingly. The suffixes ‘m’ stands for matrix and the suffixes ‘f’ for filler. ASTM D 792-13 standard was used to measure the experimental density of syntactic foams [15]. The weight and the volume of 15 mm side cube were measured to calculate the density. The volume fraction of matrix porosity (Vv) in the syntactic foams are determined by

\[
V_v = \frac{\rho_m - \rho_{ct}}{\rho_{ct}} \quad ……………………. (2)
\]

Fig. 1 is representing the experimental density, theoretical density and matrix porosity of all compositions of hybrid syntactic foam. Theoretical density showed a higher value than experimental density due to voids formed during processing. The increase in flyash cenospheres content caused an increase in matrix porosity due to surface irregularities of flyash cenospheres. These surface irregularities of flyash cenospheres causes air entrapment during mixing with vinyl ester matrix. Matrix porosity of all hybrid syntactic foams is in range of 7-10%. However, hybridization causes an increase in matrix porosity by 3%.

#### B. Impact Properties

1. Impact properties of hybrid syntactic foams with 50% total fillers

Impact strength and specific impact strength of hybrid syntactic foams with 50% total fillers.
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Plane flyash cenospheres syntactic foam (i.e. 50HSF-0-100) shows less impact strength than all hybrid syntactic foam system. Specific impact strength also follows a similar trend; with increase in flyash cenospheres vol% specific impact strength increases. The increase in impact strength is caused by an increase in high density flyash cenospheres fillers. Specific impact strength was increased by 94%, 101% and 60.8% with an increase in flyash cenospheres content by 25, 50 and 75 vol% respectively.

Fig. 3. Failure features of specimens tested under izod impact tests for 50% total fillers

Fig. 3 shows the failure features of specimens tested under unnotched Izod impact tests. This figure shows a single crack failure feature that generated from the tensile face of the specimen and was propagated towards the compression side.

Fig. 4. SEM images of 50HSF-50-50 type syntactic foam for Izod impact test at (a) 509x magnification, (b) 998x magnification

Fig. 4 (a) and (b) shows the microscopic observations (SEM) for unnotched Izod impact tests of 50HSF-50-50 type syntactic foam. It shows matrix failure, matrix-microballoon interface debonding as well as microballoon crushing at some space. SEM image shows a matrix crack and matrix–microballoon interface debonding as the failure mechanisms under the impact. matrix cracking is seen in fig. 4 (a). During impact test sample specimen breaks suddenly, because of this sudden breakage, no strain get developed in the specimen and this phenomenon leads to debonding of filler from the matrix which can be seen in fig. 4 (b).

2. Impact properties of hybrid syntactic foams with 60% total fillers

Hybrid syntactic foam system with 60% total filler volume shows a different format than 50% total filler system. For 60% total filler configuration; Impact strength of plane hollow glass microsphere syntactic foam is higher than all hybrid syntactic foams. In this hybrid syntactic foam system as the volume fraction of flyash cenospheres increases by 25% sudden drop in impact strength was observed. This behavior can be attributed to the stirring process and surface flaws of flyash cenospheres.

Impact strength further increased gradually as flyash cenospheres vol% increased to 50% and 75% respectively; however the increased impact strength is less than plane hollow glass microsphere syntactic foam. The net decrease in impact strength observed was 27%, 19.7% and 19.7% for an increase of flyash cenospheres volume fraction with 25, 50 and 75% respectively in comparison to plane hollow glass microsphere syntactic foam. This decrease in strength will be attributed to irregular surface morphology of flyash cenospheres and mechanism of fracture at high volume fraction [16]. Specific impact strength also follows similar trend; decrease in specific impact strength observed is 30%, 26%, 29% for increase in volume fraction of flyash cenospheres by 25, 50, 75 vol% respectively in hybrid syntactic foam system.

Fig. 5. Microscopic images of unnotched Izod impact tested 60HSF-50-50 type syntactic foam (a) 100x magnification, (b) 513x magnification.

Fig. 5 (a) and (b) represents the microscopic observations of unnotched Izod impact tests of 60HSF-50-50 type syntactic foam. Fig. 5 (a) shows the fractured surface of hybrid syntactic foam. while fig. 5 (b) shows microballoon crushing as the failure mechanisms under the impact. At some places aggregation of microballoons and cenosphere is observed, this also may cause a decrease in impact strength.

Fig. 6. Impact strength and specific impact strength of hybrid syntactic foams with 60% total fillers.
This aggregation of microballoons and cenosphere may be caused because of improper blending during fabrication. In hybrid syntactic foam with 60% fillers the matrix content gets reduced to 40%, this low resin content also leads to weak bonding amongst fillers and matrix. The poor bond among microballoons and matrix causes the debonding of microballoon and cenospheres.

C. Flexural properties

1. Flexural properties of hybrid syntactic foams with 50% total fillers

Fig. 8 shows the fractured specimens of different types of hybrid syntactic foams with 50% total fillers in 3-point bending configuration. Fig. 11 (a) and (b) shows SEM images of fractured surfaces of 50 HSF-50-50 hybrid syntactic foams.

The flexural strength of the neat resin was measured as 104 MPa in a previous study [17]. Flexural strength of all compositions of hybrid syntactic foams shows lower values than the neat vinyl ester resin. In plain syntactic foams, syntactic foam containing only K20 hollow glass microballoons (i.e. 50HSF-100-0) had a flexural strength of 35.86 MPa. The plane flyash cenospheres syntactic foam (i.e. 50 HSF-0-100) had a higher value than all hybrid syntactic foam system. The flexural strength of plane flyash cenospheres syntactic foam (i.e. 50 HSF-0-100) was 43.19 MPa. The flexural strength values of hybrid foams lies between these plane syntactic foams. As the vol% of fly-ash cenospheres increases 25%, 50%, 75% the flexural strength varies by -23, 1.4% and 9% respectively. The specific flexural strength of all compositions of hybrid syntactic foams shows a linear relationship with respective flexural strength. This will be attributed to a uniform density gradient. In hybrid syntactic foam system with 50% total filler, 50HSF-75-25 showed 25% decrease in specific flexural strength than their plain syntactic foam (i.e. 50HSF-100-0)

Effect of composition on flexural modulus and specific flexural modulus of hybrid syntactic foam are presented in Fig. 10. In hybrid syntactic foam with 50% total filler system, as fly cenospheres content increases by 25% (i.e. 50HSF-75-25) it showed 9% decrease in modulus than plain hollow glass microsphere syntactic foam (i.e. 50HSF-100-0). Flexural modulus increases by 4% and 23% for an increase in flyash cenospheres by 50% and 75% respectively. Specific flexural modulus for hybrid syntactic foam system is higher than neat resin. Specific flexural modulus increased with increase in flyash cenospheres content. Specific flexural modulus decreased by -11% by 25% addition of flyash cenosphere. As flyash cenospheres percentage increased by 50%, 75% in total filler content; specific flexural modulus increased by 0.2% and 16%, respectively. The stiff particles in hollow ceramic cenospheres help to improve flexural modulus. Flyash cenospheres has a higher density than K20 hollow glass spheres and will consist of thick-walled particles which lead to increase flexural modulus. Therefore an increase in flyash cenospheres vol% in the hybrid system caused an increase in flexural modulus. Effect of composition on Flexural strength and specific flexural strength of hybrid syntactic foams with 50% total fillers is shown in fig. 9.
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Fig. 10. (a) Flexural modulus and (b) specific flexural modulus of hybrid syntactic foams with 50% total fillers.

Fig. 11 (a) shows the microscopic images revealing that matrix-micro balloons debonding, matrix cracking as deformation mechanisms. The failure of the matrix should be clearly seen in fig. 11 (b).

Fig. 11. SEM images of fractured surface of 50HSF-50-50 hybrid syntactic foam in flexural testing test at (a) 509x magnification, (b) 1.00kx magnification.

2. Flexural properties of hybrid syntactic foams with 60% total fillers

Effect of composition on flexural strength and specific flexural strength of hybrid syntactic foam for 60% total filler volume are presented in Fig. 12. The flexural strength of the hybrid syntactic foam with 60% total filler volume is lower than the hybrid syntactic foam with 50% total filler volume. In plain syntactic foams with 60% filler, syntactic foam containing K20 glass micro balloons (i.e. 60HSF-100-0) had a lowest flexural strength of 22.70 MPa. The plane flyash cenospheres syntactic foam (i.e. 60 HSF-0-0) had a higher value than all hybrid syntactic foam system. The flexural strength of plane flyash cenospheres syntactic foam (i.e. 60 HSF-0-0) was 44.22 MPa.

As vol% of flyash cenospheres increases by 25%, 50%, 75% the flexural strength varies 18%, 9% and 39% respectively in comparison to plane hollow glass microballoon syntactic foam.

Effect of composition on flexural modulus and specific flexural modulus of hybrid syntactic foam with 60% total filler are presented in Fig. 13. Flexural modulus of hybrid syntactic foam increased linearly with increase in flyash cenospheres content in the hybrid system. The increase of flyash cenospheres content with higher density may leads to increase the flexural modulus but reduces flexural strength because of the stress concentration at defect present in cenospheres.

Specific flexural modulus for hybrid syntactic foam system with 60% total volume fraction is higher than neat resin. Specific flexural modulus and flexural modulus increased with increase in flyash cenospheres content. Flexural modulus increased by 17%, 33%, and 58% as flyash cenospheres percentage increased by 25%, 50%, 75% in comparison to plane hollow glass microsphere syntactic foam. Also increase in Specific flexural modulus observed by 13%, 22%, and 40% as flyash cenospheres percentage increased by 25%, 50%, 75% in comparison to plane hollow glass microsphere syntactic foam.
Fig. 13. (a) Flexural modulus and (b) specific flexural modulus of hybrid syntactic foams with 60% total fillers.

Fig. 14. Flexural Stress - strain curve of hybrid syntactic foams with 60% total fillers.

Fig. 15. SEM images of fractured surface of 60% total filler hybrid syntactic foam in flexural testing test at (a) 483x magnification, (b) 1.00kx magnification.

Fig. 16. Fractured specimens of hybrid syntactic foams in Flexural test.

V. CONCLUSIONS

The hybrid syntactic system was created by mixing glass microballoons with fly ash cenospheres in vinyl ester matrix. The impact and flexural properties hybrid syntactic foams based on glass microballoons and fly ash cenospheres were investigated. Above studies shows that the absorbed impact energy of all hybrid syntactic foams is lower than the neat resin. The impact strengths for all combinations of hybrid syntactic foam with 50% total filler shows higher impact strengths than respective combinations from 60% total filler hybrid system. However, as the flyash cenospheres content increases in the internal composition of two fillers causes the increase in impact strength. Hybrid syntactic foam shows Maximum 111% increase in impact strength in comparison to plane hollow glass microsphere syntactic foam.
The flexural strengths of hybrid syntactic foam increases with increase of fly ash cenosphere content in total filler volume fraction. Specific flexural modulus of hybrid syntactic foam system is higher than the neat resin. Specific flexural modulus increased with increase in fly ash cenospheres content. Hybrid syntactic foam shows the maximum increase of 18% in flexural modulus with a comparison to neat vinyl ester resin as well as the maximum increase of 58% in flexural modulus is observed with a comparison to plane hollow glass microsphere syntactic foam. Matrix failure and matrix-interface debonding were major fracture mechanisms led to a brittle failure of specimens and that the microballoon crushing was less significant. Fly ash cenospheres in conjunction with low density glass microballoons in 50% total filler configuration can give better performance in terms of specific impact properties and specific flexural properties than the 60% total filler based hybrid syntactic foam systems.

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