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A “rolling ball method” to make glass fiber reinforced hollow epoxy macrospheres used for three phase epoxy syntactic foam

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Glass fiber reinforced hollow epoxy macrospheres (GFR-HEMS) and hollow glass microspheres (HGMS) were used to prepare three phase epoxy syntactic foam (ESF) in this study. An innovative “rolling ball method” was implemented in the preparation of GFR-HEMS where expanded polystyrene (EPS) beads were used as initiation template. The EPS beads were coated with the epoxy resin and glass fiber using “rolling ball method”, and these coated EPS beads were later cured and post-cured at high temperature which will shrink the EPS beads thus producing a hollow macrosphere structure. The effect of volume fraction of GFR-HEMS, wall thickness of GFR-HEMS and volume fraction of HGMS on the compressive properties were discussed to find a comprehensive understanding of the structure–property relationship between the epoxy matrix and sphere fillers. Scanning electron microscope (SEM) shows that the “rolling ball method” can make glass fibers form a fiber spherical xAy network throughout the macrosphere wall, which can make GFR-HEMS and three phase ESF have great compressive strength. The ESF (570 kg/m$^3$, 27.3 MPa) can withstand the 2730 meters water pressure and provide 430 kg/m$^3$ buoyancy, which can give some advice to the preparation of buoyancy material used in deepwater oil exploration.

1. Introduction

Low density materials with high compressive strength and tolerance are often used as core materials in sandwich composites for aerospace, automotive, civil as well as marine structural applications.1 Especially in the using area of marine structural applications, the low density buoyancy materials are used to balance gravity and buoyancy of the oilfield drilling pipe. In the 1000 meters deepwater, the water pressure is about 100 atmospheres, about 100 kgf/cm$^2$. The buoyancy material needs to withstand the enormous pressure of the water while providing sufficient buoyancy. So the higher of the hydrostatic pressure resistant and the lower of the density of the buoyancy material, the better the performance of the buoyancy material.

The buoyancy materials can be classified as one phase foam, two phase foam and three phase foam. One phase foam is mainly the polymer foam such as PS foam and PU foam, but the foams have limitations because of their low compressive strength,2 so a class of closed cell syntactic foams were introduced by dispersing rigid hollow particles in a matrix.3-5 A two phase foam consists of hollow spheres dispersed in a matrix resin whereas a three phase foam consists of hollow spheres dispersed in a matrix resin containing gaseous voids or other hollow spheres.6-9

Most microspheres are made from rigid shell materials such as polymeric materials, ceramic and glass.15-25 Polymeric microspheres have limitations because of their low compressive strength (<10 MPa). Ceramic microspheres have limitations because of their high density (>0.6 g/cm$^3$). HGMS (Ø10-150 µm) have the required collapse pressure and density (20-40 MPa, 300-500 kg/m$^3$) and have actually been used in epoxy/HGMS buoyancy material.26 The density of the foam filled with only HGMS can be calculated by the following formula (1).

$$\rho_{\text{foam}} = \phi \rho_{\text{HGMS}} + (1-\phi) \rho_{\text{matrix}}$$

Here, $\rho_{\text{HGMS}}$ is 0.38 g/cm$^3$ (3M, S38HS), $\rho_{\text{matrix}}$ is about 1.12 g/cm$^3$ (Huntsman, 1564/3486 epoxy resin system), $\phi$ is the volume fraction of HGMS in the foam. In general, the $\phi_{\text{max}}$ is about 60%-70% according to “parametric theory of the random packing of particles”.27-29 When $\phi_{\text{max}}$ is 70%, $\rho_{\text{foam max}}$ is about 0.602 g/cm$^3$. In addition, when the addition volume of HGMS in the resin is high, the viscosity is so high to mix evenly and it is also very prone to produce bubbles in the composite, thus affecting the composite compressive properties. So the density of epoxy/HGMS using above raw materials is hard to reach or below 600 kg/m$^3$.

Most studies on the mechanical and fracture properties of syntactic foams are based on the maximum filler content of microspheres as this elicits the lowest possible weight of the
composites. In this study, innovative centimeter-sized GFR-HEMS with low density and high compressive strength were prepared using “rolling ball method” and used as second reinforcing sphere fillers to prepare three phase ESF used in deepwater buoyancy products. These materials were combined together using a simple casting technique. Thus it would provide different approach in the production of syntactic foam compared to previously studied foams. Centimeter-sized GFR-HEMS could further reduce the density of the syntactic foam on the basis of epoxy/HGMS composite. The macroparticle preparation method often is the secret of the marine equipment production company. The “rolling ball method” in this paper can prepare GFRAHEMS automatically using a rolling ball machine and glass fiber was added into the epoxy hollow sphere to improve the compressive strength of GFRAHEMS. And the “rolling ball method” is improved on the basis of the Samsudin method.

The study also investigates the influence of different compositions of syntactic foam on its mechanical properties. A comprehensive understanding of the structure–property relationship is lacking. Different compositions will be created by varying the types (GFR-HEMS and HGMS) and volume fraction of microspheres or macrospheres. In the three phase ESF, the effect of volume fraction of GFR-HEMS, wall thickness of GFR-HEMS and volume fraction of HGMS on the compressive properties were discussed. It is expected the interfacial adhesion between the spheres (HGMS and GFR-HEMS) and epoxy matrix could be stronger. It is also expected that GFR-HEMS and HGMS could coordinate to improve the comprehensive performance of three phase ESF.

2. Experimental

2.1 Materials

The resin used in this paper is Huntsman 1564/3486 epoxy resin system. The Huntsman Araldite® LY 1564 is a modified bisphenol-A type epoxy resin and the hardener Aradur® 3486 is a polyamine curing agent. It’s manufactured by the Huntsman Products Inc, USA. The epoxy resin 1564 is a clear liquid, and the curing agent 3486 is a clear colourless to a slightly yellow liquid. The mix ratio is 1564:3486=100:34 by weight. 1564 has the following characteristics: viscosity in the range of 1200–1400 mPa·s (ISO 1675), epoxy index (ISO 3001) is 5.8–6.05 Eq/kg. 1564 resin was chosen as the epoxyAhardener system) was injected into the tumbler during rotation and were ensured to be fully coated by the epoxy system. These beads were later added into the prepared epoxy system in proportioned quantities and were ensured to be fully coated by the epoxy system. These beads were used as intermediate materials to develop the GFR-HEMS. After that, the epoxy-coated EPS (Figure 2(a)) were transferred into a tumbler (shown in Figure 1). Then sufficient amount of glass fiber powder was supplied by Shanghai Qiyuan Packaging Technology Co., Ltd (Shanghai, China) with different range of sizes (9–10 mm, 10 kg/m³) and will be used as intermediate materials to develop the GFR-HEMS. The glass fiber powder was supplied by Hangzhou High-tech composite company, China. The size of glass fiber powder is about 300 mesh, the diameter is about 9 micrometers, the length is about 30-50 micrometers, the density is about 2.54 g/cm³.

2.2 Preparation of GFR-HEMS

GFR-HEMS were prepared by “rolling ball method”. The preparation process of GFR-HEMS can be described by Figure 1 and Figure 2. Figure 1 shows the schematic process of glass fiber reinforcing epoxy-coated EPS beads. Figure 2 shows the preparation process of GFR-HEMS.

![Figure 1 Schematic process of glass fiber reinforcing epoxy-coated EPS beads](image)

![Figure 2 Preparation process of GFR-HEMS](image)

A resin mixture comprising of clear epoxy resin (Araldite® LY 1564) and polyamine hardener (Aradur® 3486) with 3:1 ratio was formulated and mixed by using a Planetary Centrifugal Mixer (THINKY Mixer ARE-310, Japan) to produce the epoxy system uniformly without air bubbles. The EPS beads (Figure 2(a)) were later added into the prepared epoxy system in proportioned quantities and were ensured to be fully coated by the epoxy system. These beads were used as intermediate materials to develop the GFR-HEMS. After that, the epoxy-coated EPS (Figure 2(b)) were transferred into a tumbler (shown in Figure 1). Then sufficient amount of glass fiber powder (about 10 times of the mass of the epoxy-hardener system) was injected into the tumbler during rotation of the tumbler from spout 1 (shown in Figure 1) in an amount of...
injected glass fiber powder. This step is to ensure that the stickiness problem of the uncured epoxy-coated beads was addressed thus preventing the EPS beads from clumping to each other on one hand. The addition of glass fiber can also enhance the compressive strength of the epoxy macrospheres after curing on the other hand. At the same time, the tumbling rotation made the thickness of the epoxy resin on the EPS beads uniform. These coated EPS beads with glass fiber (Figure 2(c)) were then cured in an oven for 30 minutes at 50 °C and post-cured at 120 °C for 60 minutes (Figure 2(d)) to shrink all the EPS beads inside the epoxy-coated spheres with the intention to produce hollow structures within the spheres.

GFRAHEMS made above can be called 1 layer GFRAHEMS. The increasing thickness of GFRAHEMS would affect the mechanical properties of the following three phase ESF. So 2 layers GFRAHEMS and 3 layers GFRAHEMS were also prepared by the above method based on 1 layer GFRAHEMS, in order to investigate the effect of the GFRAHEMS thickness on the properties of the three phase ESF composite. In the preparation process of 2 layers GFRAHEMS, 1 layer GFRAHEMS was used as template, and the amount of epoxy-hardener-glass fiber was the same as the amount of epoxy-hardener-glass fiber for 1 layer GFRAHEMS. 2 layer GFRAHEMS was used as template in the preparation process of 3 layers GFRAHEMS.

In the preparation process of GFRAHEMS, the glass fiber used is sufficient. So the volume fraction of glass fiber almost has no change in the three kind GFRAHEMS with different layers. The volume fraction of glass fiber in GFRAHEMS is about 61.5%±2.6% tested by Thermogravimetric Analysis.

2.3 Preparation of three phase epoxy syntactic foam filled with different stacking volume fraction of GFRAHEMS

In order to study the influence of stacking volume fraction of GFRAHEMS on the compressive strength of three phase ESF, GFRAHEMS with different stacking volume fraction (100%, 80%, 60%, 40%, 20% and 0%) was added into the two-phase epoxy-HGMS composite to make three phase ESF. Figure 3 shows the preparation process of three phase ESF filled with different stacking volume fraction of GFRAHEMS.

The preparation step involves determining the amount of GFRAHEMS needed in the next experimental procedure by filling a stainless steel mould (Figure 3(a)) (Ø 65 mm*60 mm). This predetermined amount of GFRAHEMS could be thought to be 100% stacking volume of GFRAHEMS in three phase ESF (Figure 3(a)). Then the other four stacking volume fraction (80%, 60%, 40%, 20%) were formulated after calculation by weight (or by volume) showed in Figure 3(b), Figure 3(c), Figure 3(d), Figure 3(e). Epoxy-hardener, HGMS (S38HS, 3M, USA) and GFRAHEMS (1 layer, 100% stacking volume fraction) with 2:1:1 ratio were formulated after calculation. After the preparation steps have been implemented, the mixture for the matrix was prepared by mixing the epoxy resin and the hardener continuously together with the hollow glass microspheres for about 10 minutes. The amount of HGMS was fixed at 33.3% by weight (60% volume fraction of the two-phase composite) with respect to the resin mixture in order to increase the viscosity to prevent the macrospheres from floating to the surface during the foam production and further reduce the density of the target ESF. The prepared cured GFRAHEMS were added at regular intervals into the mixture subsequently after the matrix system preparation process has been completed within the duration of 10 minutes. Using such procedure, the uncured matrix compound...
consisting of GFR-HEMS dispersed in the epoxy matrix was achieved. The mixture was poured evenly into the mould and after the mixture has been transferred into the mould successfully, a constant load with standard weight (5.0 kg/cm²) was placed on top of the mould lid to maintain GFR-HEMS in their well dispersed state. All these preparation procedures are essential in ensuring that the mould will be completely filled and because the amount of GFR-HEMS was obtained in such a way that would restrict GFR-HEMS from floating to the surface during the foam production. Then the mixture was then placed in an oven at 60 °C for 30 minutes and 100 °C for 30 minutes. The composite was demoulded and then left at room temperature to complete the post curing process for 48 hours. The cured composites were cut according to standard dimensions for respective testing after 24 hours.

2.4 Preparation of three phase epoxy syntactic foam filled with different wall thickness of GFR-HEMS

In order to study the influence of wall thickness of GFR-HEMS on the compressive strength of the three phase ESF, GFR-HEMS with different wall thickness (1 layer, 2 layers, 3 layers) was added into the two-phase composite to make three phase ESF. The preparation process is the same as the preparation process showed in Figure 3. The difference is that the wall thickness is different.

2.5 Preparation of three phase epoxy syntactic foam filled with different volume fraction of HGMS in epoxy-hardener system

The volume fraction of HGMS in the epoxy system also influence the compressive strength of three phase ESF. HGMS with different volume fraction (40%, 50%, 60%, 70% and 80%) was added into epoxy-hardener system to make the two-phase mixture. Then 80% stacking volume fraction of GFR-HEMS was added into the two-phase mixture to make three phase ESF. The other preparation process is the same as the preparation process showed in Figure 3.

2.4 Characterization

ESF morphology was captured using a Nikon high definition digital camera. The density of the macrospheres was obtained by the mass divided by volume with 20 macrospheres selected randomly. The glass fiber content used in GFRAHEMS was tested by Thermogravimetric Analysis (TGA). The density of ESF was measured in accordance with ASTM D3574. Compression test of ESF was carried out using a Universal Electromechanical Tester (Instron 4465, Instron Corp., MA) in accordance with ASTM D3575. SEM morphology of ESF after compression was made using a FESEM (JEOL JEMA4701, Japan).

3. Results and discussion

3.1 Apparent analysis and density of GFR-HEMS

Figure 4 shows digital image of GFR-HEMS (2 layers). The diameter of the petri dish is 10 mm. The surfaces of GFR-HEMS are all very smooth and the GFR-HEMS are very round, which will be helpful to enhance the mechanical strength of the hollow epoxy macrosphere. The good mechanical strength will be very beneficial to enhance the mechanical strength of following ESF.

Figure 5 shows the relationship of diameter and density of GFR-HEMS. The GFR-HEMS diameter and their density distribution can be illustrated in Figure 5 where 20 reading data (3 types, total 60 data) were taken to ensure a good representation of the overall GFR-HEMS morphology. It can be seen that the diameter distribution of GFR-HEMS is between 9 mm to 11.2 mm. From Figure 5, it can be seen that the GFR-HEMS density is mainly distributed in three regions. (a) GFR-HEMS-1 layer, 0.18-0.35 g/cm³ (diameter 9.0-10.2 mm), (b) GFR-HEMS-2 layers 0.41-0.58 g/cm³ (diameter 9.8-11.0 mm), (c) GFR-HEMS-3 layers 0.51-0.70 g/cm³ (diameter 10.1-11.0 mm), showing that the bigger the diameter of the macrosphere, the thicker the wall thickness of the macrosphere, the higher the density of the macrosphere. The thicker macrospheres are more helpful to improve the compressive strength, but not good to reduce the density of the syntactic foam to a certain extent. So when choosing hollow spheres as filler, a balance of the strength and the density of the composite is needed in order to achieve the goal of “high strength and low density”. The average density of GFR-HEMS can be calculated by formula (2).

\[ \rho_{GFR-HEMS} = \frac{\sum_{n=1}^{20} (m_n)_{GFR-HEMS}}{\sum_{n=1}^{20} (V_n)_{GFR-HEMS}} \]  

The average density of GFR-HEMS (\( \rho_{GFR-HEMS} \)) is the ratio of the mass of all the GFR-HEMS balls (\( \sum_{n=1}^{20} (m_n)_{GFR-HEMS} \)) to the volume of all the GFR-HEMS balls (\( \sum_{n=1}^{20} (V_n)_{GFR-HEMS} \)), and the average densities are 0.24 g/cm³ (1 layer), 0.48 g/cm³ (2 layers) and 0.65 g/cm³ (3 layers), respectively.

The EPS beads were supplied with different range of sizes (9–10 mm, 10 kg/m³) and was used as intermediate materials to develop the GFR-HEMS. If the size of the EPS templates are completely consistent, the more the layer, the thicker the sphere wall of the GFR-HEMS, and the bigger the diameter of GFR-HEMS, the bigger the density of GFR-HEMS. But the size of the EPS templates are not entirely consistent from 9-10 mm, so Figure 5 can be used to show
the changing trend of the density with the increasing diameter. And through Figure 5, the average density can give some guidance to prepare three phase epoxy syntactic foam, especially in reducing the final foam density.

3.2 Thermogravimetric analysis of the glass fiber content used in GFR-HEMS

![Figure 6 TG curves of GFR-HEMS with different layers](image)

The glass fiber content used in GFR-HEMS has been tested by Thermogravimetric analysis (TGA). The TGA data were obtained in air atmosphere at a heating rate of 50 °C/min with a Netzsch TG-209 F3 thermogravimetric analyzer (NETZSCH, Germany). In each case, about 50 mg GFR-HEMS sample was examined under the gas flow rate of 20 mL/min at the temperatures ranging from 50 to 700 °C to evaluate the glass fiber content in GFR-HEMS. Figure 6 shows TG curves of GFR-HEMS with different layers. The glass fiber volume fraction (Øgf) can be calculated by formula (3).

\[
\phi_{GF} = \frac{\rho_{GF}}{\rho_{VGF} + \rho_{Epoxy system}} = \frac{m_{GF}}{\rho_{GF} \cdot V_{GFR-HEMS}}
\]

Here, \(\rho_{GF}\) is 2.54 g/cm\(^3\) (Hangzhou High-tech composite company, China), \(\rho_{Epoxy system}\) is about 1.12 g/cm\(^3\) (Huntsman, 1564/3486 epoxy resin system), \(\phi_{GF}\) is the volume fraction of GF in GFR-HEMS. The calculation data can be summarized in table 1.

<table>
<thead>
<tr>
<th>GFR-HEMS kind</th>
<th>GF content (wt%)</th>
<th>ØGF (v%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 GFR-HEMS 1 layer</td>
<td>80.2</td>
<td>64.1</td>
</tr>
<tr>
<td>2 GFR-HEMS 2 layers</td>
<td>77.9</td>
<td>60.9</td>
</tr>
<tr>
<td>3 GFR-HEMS 3 layers</td>
<td>76.8</td>
<td>59.4</td>
</tr>
<tr>
<td>Average data</td>
<td>61.5±2.6</td>
<td></td>
</tr>
</tbody>
</table>

In the preparation process of GFR-HEMS, the glass fiber used is sufficient. So the volume fraction of glass fiber almost has no change in the three kind GFR-HEMS with different layers seen from Figure 6 and Table 1. The volume fraction of glass fiber in GFR-HEMS is about 61.5±2.6%. The density of GFR-HEMS sphere wall can be calculated by formula (4).

\[
\rho_{sphere\ wall} = \phi_{GF} \cdot \rho_{GF} + (1 - \phi_{GF}) \cdot \rho_{Epoxy\ system}
\]

Here, \(\rho_{GF}\) is 2.54 g/cm\(^3\), \(\rho_{Epoxy\ system}\) is about 1.12 g/cm\(^3\) (1564/3486 epoxy system), \(\phi_{GF}\) is about 61.5%, so \(\rho_{sphere\ wall} = 0.615\times2.54 + (1-0.615)\times1.12 = 1.99\) g/cm\(^3\). The data can be used to predict the sphere wall thickness of GFR-HEMS (\(T_{sphere\ wall}\)) combined with the average measured density of GFR-HEMS (Figure 5). The prediction formula is shown in formula (5).

\[
T_{sphere\ wall} = \frac{\rho_{sphere\ wall} \cdot V_{sphere\ wall}}{\rho_{GFR-HEMS}} = \frac{\rho_{sphere\ wall} \cdot \frac{4}{3} \pi (r_{outer})^3 - \frac{4}{3} \pi (r_{inner})^3}{\rho_{GFR-HEMS}}
\]

Here, the mass of the EPS bead is ignored. The size of the EPS beads used to prepare GFR-HEMS is about 9-10 mm. So the average diameter of EPS beads can be assumed as 9.5 mm or 0.95 cm. The average radius \(r_{sphere}\) is about 0.95 cm/2 = 0.475 cm. \(\rho_{GFR-HEMS}\) are 0.24 g/cm\(^3\) (1 layer), 0.48 g/cm\(^3\) (2 layers) and 0.65 g/cm\(^3\) (3 layers), respectively. \(\rho_{sphere\ wall}\) is about 1.99 g/cm\(^3\) from above calculation (formula (4)). The thicknesses of sphere wall of GFR-HEMS (\(T_{sphere\ wall}\)) are summarized in Table 2.

<table>
<thead>
<tr>
<th>GFR-HEMS kind</th>
<th>(r_{inner}) (cm)</th>
<th>(\rho_{sphere\ wall}) (g/cm(^3))</th>
<th>(\rho_{GFR-HEMS}) (g/cm(^3))</th>
<th>(T_{sphere\ wall}) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 GFR-HEMS 1 layer</td>
<td>0.475</td>
<td>1.99</td>
<td>0.24</td>
<td>0.0208 (208 μm)</td>
</tr>
<tr>
<td>2 GFR-HEMS 2 layers</td>
<td>0.475</td>
<td>1.99</td>
<td>0.48</td>
<td>0.0458 (458 μm)</td>
</tr>
<tr>
<td>3 GFR-HEMS 3 layers</td>
<td>0.475</td>
<td>1.99</td>
<td>0.65</td>
<td>0.0669 (669 μm)</td>
</tr>
</tbody>
</table>

The data shows the prediction thicknesses of sphere wall of GFR-HEMS. But this data are not the real data, they need to be carefully validated with real data. SEM images can give us the intuitive visual data.

3.3 Microstructure analysis of GFR-HEMS and epoxy syntactic foam

SEM experiments have been done to find the sphere wall thickness changing trend of GFR-HEMS in the foam. In the sample preparation process, the samples were randomly selected and carried out for SEM test. Figure 7 shows SEM of three phase ESF with different layer GFR-HEMS. It can been seen that the wall thickness of different layer GFR-HEMS is different, but the total trend seen from Figure 7 that the thickness is increasing with the increasing layers. In addition, the thickness of the same layer GFR-HEMS is also different seen from Figure 7 that the use of the layer to classify GFR-HEMS. And the density of GFR-HEMS is also measured by the average density. The thicknesses of sphere wall of GFR-HEMS in ESF are summarized in Table 3.

From Table 3, it can be seen that the average thickness calculated by formula (5) almost is the same as the average thickness from SEM. This means that that the calculations are correct. The calculation is based on the data from Figure 5. So Figure 5 can not only be used to show the changing trend of the density with the increasing diameter, but also can give us some guidance to prepare three phase epoxy syntactic foam, especially in reducing the final foam density.
Some of the layers (as shown in the SEM in Figure 7) that seem very homogeneous and indeed is playing an important role in enhancing the compressive strength of the foam. The cellular structure developed in the matrix can give more lightweight structure in the foam, so the structure is also important in reducing the density of the foam. Therefore it needs to be taken into account as a void/cellular structure and its characterization is important as has a major impact in the final compressive strength and the density of the foam.

In addition, it also can be seen that there is almost no interfacial between the two phases (sphere wall and epoxy-HGMS system) in all the SEM mages in Figure 7. The combination of sphere wall phase and epoxy-HGMS system phase is closely. In the section of mechanical enhancement mechanism of GFR-HEMS in ESF, Figure 7(b2) will be carefully discussed as a representative in section 11.

3.4 Macrostructure analysis of epoxy syntactic foam

Figure 8 Digital image of ESF showing matrix porosity, GFR-HEMS and PS particles

Figure 8 shows digital image of ESF showing matrix porosity, GFR-HEMS and PS particles. The image shows a typical microstructure of epoxy syntactic foam prepared in this study. The hollow spheres are dispersed randomly in the foam. The foam is cut into two parts, not all the GFR-HEMS are cut from the middle, so the cellular structure exhibits a very heterogeneous morphology. The inner walls of the hollow epoxy macrospheres are all very neat and smooth because of the role of the EPS bead templates. Regular spherical wall can increase the compressive strength of the macrospheres. Two types of porosity appeared in the foam, which were contributed by the hollow epoxy macrospheres and matrix (epoxy+HGMS). The hollow epoxy macrosphere porosity can be controlled by selecting the type and the size of hollow epoxy macrosphere. However, the matrix porosity could be attributed to air entrapment, which resulted in the formation of voids within the matrix during the mixing and coating procedure.

Although an increase in porosity would undermine the mechanical properties of the foam system, which can also be considered an advantage to adjust the overall density and properties of the system. Epoxy syntactic foam contains GFR-HEMS and HGMS in the epoxy matrix. HGMS added in the epoxy matrix can increase the viscosity of the matrix to hinder the floating of GFR-HEMS. So GFR-HEMS can be uniformly dispersed in the matrix resin in the curing process.
ESF can be used as buoyancy materials to offset the gravity of oil pipe and other equipments used in the deepwater oil exploration.

3.5 Influence of stacking volume fraction of GFR-HEMS on the compressive properties of three phase epoxy syntactic foam

![Figure 9 Influence of stacking volume fraction of GFR-HEMS on the compressive properties of three phase ESF (volume fraction of HGMS in the epoxy system is 60%). Stacking volume fraction of GFR-HEMS in the mould are 20%, 40%, 60%, 80% and 100%, respectively.)](image)

Figure 9 shows influence of stacking volume fraction of GFR-HEMS on the compressive properties of three phase ESF. When volume fraction of HGMS in the epoxy system is 60%, the compressive strength of three phase ESF decreases with the increasing GFR-HEMS content from 61.4 MPa (0% GFR-HEMS) to 52.0 MPa (20% GFR-HEMS), 33.0 MPa (40% GFR-HEMS), 31.4 MPa (60% GFR-HEMS), 26.0 MPa (80% GFR-HEMS) and 25.9 MPa (100% GFR-HEMS), respectively. Several conclusions can be obtained from analysis of the above data.

(a) The compressive strength of three phase ESF (Figure 9) are 52.0 MPa (20%), 33.0 MPa (40%), about 84.7% (52.0/61.4) and 53.7% (33.0/61.4) of the ESF without GFR-HEMS (0%, epoxy-HGMS composite), respectively, indicating that the 40% addition of GFR-HEMS already make the compressive strength of three phase ESF reach the percolation point. The rapid reduction of compressive strength of three phase ESF is induced by the increasing defects in the composite because of the addition of GFR-HEMS. The defects can be showed in Figure 8 above. Seen from Figure 8, the defects includes the GFR-HEMS itself, matrix porosity, HGMS and the contact interface between GFR-HEMS and epoxy-hardener-HGMS system. (a1) The contact interface between GFR-HEMS and epoxy-hardener-HGMS system increases with the increasing GFR-HEMS content, and the matrix porosity may also increases with the increasing GFR-HEMS content in the mixing progress because of the air intervention. (a2) In addition, the percolation theory can be used to explain the mechanical strength changing trend. Figure 10 shows the dispersion model of GFR-HEMS spherical filler in the epoxy-hardener-HGMS system. Before the percolation point of GFR-HEMS in the foam (Figure 10(a)), there is almost no contact between the hollow spheres. There is almost no contact defect. The compressive strength is kept at a high level (52.0 MPa), and only a little lower than that of the foam with GFR-HEMS (61.4 MPa). Figure 10(b) shows 40% GFR-HEMS dispersion state in the epoxy-hardener-HGMS system. The contact rate of GFR-HEMS contacting with each other increases rapidly after exceeding percolation point (Figure 10(b)), compressive strength will decrease rapidly because of GFR-HEMS contact. The above defects make compressive strength of three phase ESF decrease with the increasing GFR-HEMS. After the percolation point of GFR-HEMS in the foam (take 100% (Figure 10(c) for example), there are so many contact defects between GFR-HEMS. The compressive strength will decrease gradually with the increasing GFR-HEMS contact defects.

(b) Compressive strength of three phase ESF are 31.4 MPa (60%), 26.0 MPa (80%) and 25.9 MPa (100%), about 51.1% (31.4/61.4), 42.3% (26.0/61.4) and 42.2% (25.9/61.4) of the ESF without GFR-HEMS (0%, epoxy-HGMS composite), respectively. The reducing trend of compressive strength becomes flat gradually, and compressive strength data basically maintain at the steady decline curve. Compressive strength (80%) and compressive strength (100%) are almost the same, showing that compressive strength almost is not influenced by GFR-HEMS content. So in order to maintain sufficient compressive strength at the same time, get enough large buoyancy at low density, the more the GFR-HEMS content added in three phase ESF means the better the buoyancy properties which includes high compressive strength and low density. 100% GFR-HEMS content added in three phase ESF is the best state to get enough buoyancy at this time.

3.6 Influence of wall thickness of GFR-HEMS on the compressive properties of three phase epoxy syntactic foam

Not only stacking volume fraction of GFR-HEMS influences compressive strength of three phase ESF, wall thickness of GFR-HEMS also influences compressive strength of three phase ESF. Figure 11 shows influence of wall thickness of GFR-HEMS on compressive strength of three phase ESF. From above section (3.3), compressive strength of three phase ESF (2 layers) decreases with the increasing GFR-HEMS content, compressive strength of three phase ESF (1 layer and 3 layers) also have the same changing trend. In addition, one clear phenomenon can be found that compressive strength of three phase ESF (3 layers) is the highest in all the three samples with the same stacking volume fraction of GFR-HEMS in three phase ESF, compressive strength of three phase ESF (2 layers) is the second, and compressive strength of three phase ESF (1 layer) is the lowest. The above phenomenon indicates that compressive strength of three phase ESF increases with the increasing wall thickness of GFR-HEMS (layers) filled in the ESF.
With the stacking volume fraction of GFR-HEMS for 20% as an example, compressive strength of three phase ESF increases from 41.3 MPa (1 layer), 52.0 MPa (2 layers) and 57.8 MPa (3 layers), about 67.3% (41.3/61.4, 1 layer), 84.7% (52.0/61.4, 2 layers) and 94.1% (57.8/61.4, 3 layers) of the ESF without GFR-HEMS, respectively, showing that GFR-HEMS with higher wall thickness not only can be used to improve the sphere itself strength but also improve the strength of three phase ESF.

When the stacking volume fraction of GFR-HEMS is 100%, compressive strength of three phase ESF increases from 16.9 MPa (1 layer), 25.9 MPa (2 layers) and 31.0 MPa (3 layers), respectively, showing that the wall thickness of GFR-HEMS influences the compressive strength clearly. So in order to maintain sufficient compressive strength, the thicker the wall of GFR-HEMS means the better the compressive strength. But at the same time, the density of three phase ESF which is related to the buoyancy property should be also concerned.

Figure 12 shows influence of wall thickness of GFR-HEMS on compressive deformation rate of three phase ESF. Seen from Figure 12, it can conclude that the deformation rate and compressive strength of three phase ESF have the same changing trend not only at low stacking volume fraction but also at high stacking volume fraction of GFR-HEMS in the composite, all increase with the increasing GFR-HEMS wall thickness. When the stacking volume fraction of GFR-HEMS in the composite is at 20%, the deformation rate increase from 4.95% (1 layer) to 5.59% (2 layers) and 6.09% (3 layers), respectively. Although the data deformation changing rate is small, it also indicates that the increasing GFR-HEMS wall thickness not only increases the anti-deformation ability of GFR-HEMS itself, but also increases the anti-deformation ability of three phase epoxy syntactic foam.

### 3.7 Influences of stacking volume fraction of GFR-HEMS and wall thickness of GFR-HEMS on the density of three phase epoxy syntactic foam

The main purpose of using centimeter-sized lightweight epoxy hollow sphere GFR-HEMS in ESF is in order to ensure the strength of the three phase material at the same time, as far as possible to reduce the density of three phase ESF, so as to improve the buoyancy compensation ability of three phase ESF. Figure 13 shows influences of stacking volume fraction of GFR-HEMS and wall thickness of GFR-HEMS on the density of three phase ESF. Seen from Figure 13(a), the density of three phase ESF decreases with the increasing GFR-HEMS (1 layer) volume fraction from 0.676 g/cm³ (0%) to 0.62 g/cm³ (20%), 0.58 g/cm³ (40%), 0.55 g/cm³ (60%), 0.48 g/cm³ (80%) and 0.46 g/cm³ (100%), respectively. When the density of three phase ESF are 0.58 g/cm³ (40%) and 0.48 g/cm³ (80%), compressive strength are 26.4 MPa (40%) and 17.6 MPa (80%), respectively, showing that the density decreases with increasing GFR-HEMS content, compressive strength also decreases with increasing GFR-HEMS content.

When the lightweight composite is used as buoyancy material, the lower the density the better the buoyancy properties when the compressive strength is kept constant. On the other side, the higher the compressive strength the better the buoyancy properties when the density is kept constant. Higher compressive strength and lower density are often contradictory in buoyancy material, so one balance should be found between them in order to achieve the best combination of “high strength and low density”.

The density changing trend with the increasing stacking volume fraction of GFR-HEMS (2 layers, Figure 13(b)) is the same as the density changing trend (1 layer). The density (2 layers) decreases with the increasing GFR-HEMS content from 0.676 g/cm³ (0%) to 0.67 g/cm³ (20%), 0.64 g/cm³ (40%), 0.63 g/cm³ (60%), 0.60 g/cm³ (80%) and 0.58 g/cm³ (100%), respectively, all higher than the density (1 layer) with the same content, showing that the higher thickness of GFR-HEMS makes the three phase ESF have higher density. But only when the GFR-HEMS stacking volume fraction (2 layers) is higher than 80%, the density will be reduced to below 0.6 g/cm³, the corresponding compressive strength are 26.0 MPa (80%) and 25.9 MPa (100%), respectively, higher than the compressive strength of three phase ESF filled with 1 layer GFR-HEMS.

Adding two layers of hollow spheres can improve the compressive strength of the composite, but also increase the density of the composite, which reduces the buoyancy compensation ability of the composite materials. In this case, the maximum content of GFR-HEMS should be added into the composite to reduce the density of the three phase ESF. 100% stacking volume fraction of GFR-HEMS is the best choice.
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3.8 Influence of HGMS content in the epoxy-hardener system on the compressive strength of three phase epoxy syntactic foam

Figure 14 shows influence of volume fraction of HGMS in the epoxy-hardener system on the compressive properties of three phase ESF. When stacking volume fraction of GFR-HEMS in the mould is 80%, the compressive strength of three phase ESF increases with the increasing HGMS volume fraction in the epoxy-hardener system from 20.5 MPa (40%) to 23.9 MPa (50%), 26.0 MPa (60%), 27.4 MPa (70%), and then decreases to 15.1 MPa (80%).

Especially when the HGMS content in the epoxy-hardener system is low, floating phenomenon of GFR-HEMS is very easy to occur in the curing process of thermosetting epoxy resin because of lower density of GFR-HEMS and low viscosity of the epoxy system at the same time. The wall thickness of GFR-HEMS should be less than 3 layers. 100% stacking volume fraction of GFR-HEMS (2 layers) may be a good choice to make three phase ESF have good comprehensive performances. The corresponding compressive strength and density are 25.9 MPa and 0.58 g/cm³, respectively. The compressive strength and density of three phase ESF studied by Samsudin et al. are 19.7 MPa and 0.566 g/cm³, respectively. From the data above, one can conclude that the three phase ESF has better comprehensive performances in this study. 25.9 MPa and 0.58 g/cm³ are the best combination of “high strength and low density” in this study.

3.8 Influence of HGMS content in the epoxy-hardener system on the compressive strength of three phase epoxy syntactic foam

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Figure 13 Influences of stacking volume fraction of GFR-HEMS and wall thickness of GFR-HEMS on the density of three phase ESF (volume fraction of HGMS in the epoxy-hardener system is 60%). Stacking volume fraction of GFR-HEMS in the mould are 20%, 40%, 60%, 80% and 100%, respectively.

Because the density of GFR-HEMS (3 layers) is 0.65 g/cm³, the same as that of two-phase Epoxy-HGMS composite (0.676 g/cm³), the density of three phase ESF distributes between 0.67 g/cm³ and 0.68 g/cm³, almost has no change after adding GFR-HEMS from Figure 13(c), showing that the addition of GFR-HEMS has no effect on reducing the density of the composite. At the same time, the addition of GFR-HEMS increases the defects of three phase ESF, which decreases the compressive strength of three phase ESF with the increasing GFR-HEMS content. In addition, the addition of GFR-HEMS also makes the ESF preparation process be complicated and increases the preparation cost. The compressive strength of three phase ESF (3 layers GFR-HEMS) all higher than that of three phase ESF (2 layers and 1 layer GFR-HEMS) from the above compressive strength data. But the addition of GFR-HEMS (3 layers) has no effect on reducing the density of three phase ESF, so it is limited to reduce the density of three phase ESF through increasing GFR-HEMS layers and get higher compressive strength at the same time.

It can conclude that increasing stacking volume fraction of GFR-HEMS (1 layer and 2 layers) can reduce the density of three phase ESF. In addition, increasing wall thickness of GFR-HEMS can increase compressive strength of three phase ESF, but increase the density of ESF at the same time. It is limited to increase compressive strength through increasing the wall thickness of GFR-HEMS, and maintain low density at the same time. The wall thickness of GFR-HEMS should be less than 3 layers. 100% stacking volume fraction of GFR-HEMS (2 layers) may be a good choice to make three phase ESF have good comprehensive performances. The corresponding compressive strength and density are 25.9 MPa and 0.58 g/cm³, respectively. The compressive strength and density of three phase ESF studied by Samsudin et al. are 19.7 MPa and 0.566 g/cm³, respectively. From the data above, one can conclude that the three phase ESF has better comprehensive performances in this study. 25.9 MPa and 0.58 g/cm³ are the best combination of “high strength and low density” in this study.

3.8 Influence of HGMS content in the epoxy-hardener system on the compressive strength of three phase epoxy syntactic foam

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Figure 13 Influences of stacking volume fraction of GFR-HEMS and wall thickness of GFR-HEMS on the density of three phase ESF (volume fraction of HGMS in the epoxy-hardener system is 60%). Stacking volume fraction of GFR-HEMS in the mould are 20%, 40%, 60%, 80% and 100%, respectively.

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It can conclude that increasing stacking volume fraction of GFR-HEMS (1 layer and 2 layers) can reduce the density of three phase ESF. In addition, increasing wall thickness of GFR-HEMS can increase compressive strength of three phase ESF, but increase the density of ESF at the same time. It is limited to increase compressive strength through increasing the wall thickness of GFR-HEMS, and maintain low density at the same time. The wall thickness of GFR-HEMS should be less than 3 layers. 100% stacking volume fraction of GFR-HEMS (2 layers) may be a good choice to make three phase ESF have good comprehensive performances. The corresponding compressive strength and density are 25.9 MPa and 0.58 g/cm³, respectively. The compressive strength and density of three phase ESF studied by Samsudin et al. are 19.7 MPa and 0.566 g/cm³, respectively. From the data above, one can conclude that the three phase ESF has better comprehensive performances in this study. 25.9 MPa and 0.58 g/cm³ are the best combination of “high strength and low density” in this study.

3.8 Influence of HGMS content in the epoxy-hardener system on the compressive strength of three phase epoxy syntactic foam

Figure 14 shows influence of volume fraction of HGMS in the epoxy-hardener system on the compressive properties of three phase ESF. When stacking volume fraction of GFR-HEMS in the mould is 80%, the compressive strength of three phase ESF increases with the increasing HGMS volume fraction in the epoxy-hardener system from 20.5 MPa (40%) to 23.9 MPa (50%), 26.0 MPa (60%), 27.4 MPa (70%), and then decreases to 15.1 MPa (80%). The phenomenon can be illustrated by structure characteristics of the digital images in Figure 15. Figure 15 shows digital image of three phase epoxy syntactic foam.

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high temperature, leading to the delamination phenomenon of three phase ESF. The lower the HGMS content in the epoxy-hardener system, the more obvious the floating phenomenon, the more obvious the delamination phenomenon of three phase ESF. Seen from Figure 15, there are no GFR-HEMS at the bottom of the samples (40% and 50%) and the delamination phenomenon of three phase ESF is the most obvious in the five samples. There almost is no delamination phenomenon in the three phase ESF (60% sample) and the GFR-HEMS disperse uniformly in the matrix. The higher viscosity of the epoxy-HGMS system (60%) can prevent the floating phenomenon.

Figure 15 Digital image of three phase ESF (volume fraction of HGMS in the epoxy-hardener system are 40%, 50%, 60%, 70% and 80%, respectively. Stacking volume fraction of GFR-HEMS in the mould is 80%)

With the increasing HGMS volume fraction in the epoxy system, the compressive strength of three phase ESF increases to 27.4 MPa (70%), which is the highest compressive strength. But HGMS filled in epoxy system is limited, $\Phi_{\text{max}}$ will appear and $\Phi_{\text{max}}$ is about 60%-70% according to “parametric theory of the random packing of particles” from previous analysis in introduction.27-29 After $\Phi_{\text{max}}$, HGMS are in contact with each other and HGMS would rupture under the pressure in the preparation process, then the compressive strength of three phase ESF decreases to 15.1 MPa (80%). So in the three phase ESF, HGMS content in the epoxy-hardener system is not the higher the better. Proper HGMS content should be considered in the preparation process of three phase ESF. Here 60 v% of HGMS in the epoxy-hardener system may be the proper choice.

3.9 Influence of HGMS content in the epoxy-hardener system on the density of three phase epoxy syntactic foam

![Figure 16](image)

Figure 16 Influences of volume fraction of HGMS in the epoxy-hardener system on the density of three phase ESF (volume fraction of HGMS in the epoxy-hardener system are 40%, 50%, 60%, 70% and 80%, respectively. Stacking volume fraction of GFR-HEMS in the mould is 80%)

Figure 16 shows influences of volume fraction of HGMS in the epoxy-hardener system on the density of three phase ESF. From Figure 16, it can be seen that the density of three phase ESF decreases with the increasing HGMS content from 0.68 g/cm$^3$ (40%) to 0.64 g/cm$^3$ (50%), 0.60 g/cm$^3$ (60%), 0.55 g/cm$^3$ (70%) and 0.47 g/cm$^3$ (80%), showing that adding HGMS is useful to reduce the density of three phase ESF and provide greater buoyancy. The effect of adding HGMS and adding GFR-HEMS are equally important to reduce the density of three phase ESF. Although great addition of HGMS greatly reduces the density of three phase ESF, the other properties such as compressive strength should also be considered. The adding content of HGMS needs comprehensive consideration of the ESF properties. Here 60% is lower than the maximum volume fraction of HGMS in the epoxy system, and the viscosity of the mixture is also proper to add GFR-HEMS in the mixture, this is why 60% volume fraction addition of HGMS is chosen to add different content of GFR-HEMS above.

3.10 Mechanical rupture behaviour of epoxy syntactic foam

In order to know the rupture process of three phase ESF in the universal testing machine during the compression process, the cured big epoxy syntactic foam (300 mm*300 mm) was cut into small squares (60 mm *60 mm *60 mm) to do the compression test. Compressive strength-stain curve of ESF is shown in Figure 17. The compressive strength of the syntactic foam is about 27.3 MPa, about 2730 meters water pressure, which is almost the same as the compressive strength of the syntactic foam using cylinder sample as a test specimen above (25.9 MPa). The compressive strength data is in the range of measurement error.

![Figure 17](image)

Figure 17 Compressive strength-stain curve of ESF (volume fraction of HGMS in the epoxy system is 60%. Stacking volume fraction of GFR-HEMS (2 layers) in the mould is 100%.)

The compressive behaviour displayed by the syntactic foam was comparable to other syntactic foam systems, which utilized other thermoset matrix and glass microspheres as their constituents.2 The compressive strength drop at 4.4% can be related to the occurrence of crack initiation in the matrix as can be seen from the progressive cell collapse image included in Figure 17.35 At this stage, compression of the material resulted in a filling up of the matrix porosity due to the rupture of the porous feature. Further compression caused the formation of a shear crack in the longitudinal direction (i.e. the direction of compression).2 The longitudinal crack grew quickly after the crack beginning in several seconds. At this stage, further compression of the material resulted in
more filling up of the matrix porosity due to the rupture of the porous feature. The fracture mechanism in this region involved crushing of the GFR-HEMS, and similar observations were also reported by Kim, Ming Yu and so on.\textsuperscript{37,39} Besides sphere crushing, the failure of GFR-HEMS can also be attributed to debonding (i.e. interfacial fracture between the matrix and GFR-HEMS) at the surfaces of the GFR-HEMS. However, the presence of voids in the GFR-HEMS limits the occurrence of debonding and promoted a higher failure mechanism through the rupture of the sphere wall because such fracture is faster than debonding. In addition, seen from Figure 17, most of the GFR-HEMS are intact, showing the prevention effect of GFR-HEMS on the cracking of the foam.

The average density of the syntactic foam system is about 570 kg/m\textsuperscript{3}, providing about 430 kg/m\textsuperscript{3} buoyancy when the ESF is used in the deepwater oil exploration. The syntactic foam with the same structure has been used in deepwater oil explorations showed in United States Patent (NO: US 7121767 B1, Rugged foam buoyancy modules and method of manufacture) and the Buoyancy product of BalmoralOffshore company and other companies. The lower density is due to the utilization of the GFR-HEMS and HGMS, which can effectively reduce the density of the foam and also provide a way of reducing the production cost which is attributed to the low price of the EPS bead templates and glass fiber compared to the other type hollow spheres available in the market.

3.11 Mechanical enhancement mechanism of GFR-HEMS in ESF

Figure 18 shows SEM of three phase ESF (GFR-HEMS-2 laymers)

Figure 18 shows SEM of three phase ESF. Seen from Figure 18, the matrix resins of the sphere wall and epoxy-HGMS system are all the same kind epoxy system (Huntsman 1564/3486 epoxy resin system). There is almost no interfacial between the two phases (sphere wall (b) and epoxy-HGMS system(c)). The combination of b phase and c phase is closely. Interfacial fracture between the epoxy-HGMS system and GFR-HEMS is not so easy to happen. This can be illustrated by the long the longitudinal crack in Figure 17. The hollow spheres are destroyed by longitudinal crack, and there is almost no denting phenomenon occurrence in Figure 17, and similar observations were also reported by Samsudin.\textsuperscript{37} The presence of voids in the GFR-HEMS limits the occurrence of debonding and promoted a higher failure mechanism through the rupture of the sphere wall because such fracture is faster than debonding.\textsuperscript{38,39}

The sphere inner surface (Figure 18(a)) of GFR-HEMS keeps a good radian because of the effect of the EPS bead, which will make GFR-HEMS transfer force along the sphere surface when GFR-HEMS is pressed by external force. In the sphere wall (Figure 18(b)), glass fiber dispersed uniformly in the epoxy matrix and glass fiber and epoxy resin are closely bonded together, showing that “rolling ball method” is a very appropriate method to make glass fiber reinforced epoxy resin in the macrosphere preparation process. The thickness of the macrosphere wall is about 457 µm and the thickness distribution is also very uniform. These are because the centrifugal force & the pressure of rolling ball machine can make glass fiber uniformly disperse in epoxy resin and ensure that the sphere wall thickness is uniform.

The forces (the centrifugal force & the pressure) can also make glass fibers form a fiber spherical x-y network throughout the macrosphere epoxy matrix. Almost all of the fiber direction in the network are vertical to sphere center direction (diameter direction, z-direction) in Figure 18(b). When GFR-HEMS are used in three phase ESF, the structure of fiber spherical x-y network can make GFR-HEMS and three phase ESF have great compressive strength.

Figure 19 shows mechanical enhancement mechanism of GFR-HEMS

Figure 19 shows mechanical enhancement mechanism of GFR-HEMS. When GFR-HEMS are pressed by the forces from the different directions in the composite, forces can be decomposed into forces in different directions by the spherical structure. When GFR-HEMS is under isostatic pressure, the forces can be considered equal, so $F_1 = F_2 = F_3 = F_4 = F_5 = F_6 = F_7 = \ldots = F_n$ and then $F_{ij} = F_{22}$, $F_{33} = F_{44} = F_{55} = F_{66} = F_{77} = F_{88} = F_{99} = \ldots = F_{61}$ in Figure 19. The divided forces can transfer through the glass fiber spherical x-y network of GFR-HEMS, so most of the forces can be offset. Only a very small force transfers along the axial direction (z-direction), so it needs tremendous pressure to destroy GFR-HEMS. These are reasons why three phase ESF has so higher compressive strength.

4. Conclusions

The prepared GFR-HEMS using “rolling ball method” showed great potential in replacing HGMS, due to its simple production method and low cost production strategy because it does not utilize any expensive specialized equipment during its processing procedure which can be implemented at ambient temperature. The preparation
of ESF/GFR-HEMS/HGMS syntactic foams and their compressive properties were investigated in the present study. The main conclusions can be summarized as followed.

(a) “Rolling ball method” can make glass fibers form a fiber spherical x-y network throughout the macrosphere to make GFR-HEMS and three phase ESF have great compressive strength. The produced ESF has relatively high compressive strength and low density, thus has the potential to be used in the deepwater oil exploration.

(b) The compressive strength of three phase ESF (HGMS, 60%) decreases with the increasing GFR-HEMS stacking volume fraction, which is induced by the increasing defects in the composite. The defects includes the GFR-HEMS itself, matrix porosity, HGMS and the contact interface between GFR-HEMS and epoxy-hardener-HGMS system. In order to maintain sufficient compressive strength at the same time, get enough large buoyancy at low density, the more the GFR-HEMS content added in three phase ESF means the better the buoyancy properties. 100% GFR-HEMS content added in three phase ESF is the best state to get enough buoyancy at this time.

(c) When the stacking volume fraction of GFR-HEMS is 100%, the compressive strength of three phase ESF increases from 16.9 MPa (1 layer), 25.9 MPa (2 layers) and 31.0 MPa (3 layers), respectively, showing that the wall thickness of GFR-HEMS influences the compressive strength clearly. The thicker the wall of GFR-HEMS means the better the compressive strength. It is limited to increase compressive strength through increasing the wall thickness of GFR-HEMS, and maintain low density at the same time. The wall thickness of GFR-HEMS should be less than 3 layers. 100% stacking volume fraction of GFR-HEMS (2 layers) may be a good choice to make three phase ESF have good comprehensive performances.

(d) With the increasing HGMS volume fraction in the epoxy-hardener system, the compressive strength of three phase ESF increases to 27.4 MPa (70%), and then decreases to 15.1 MPa (80%). So in the three phase ESF, HGMS content in the epoxy-hardener system is not the higher the better. The mixture material viscosity should be considered in the preparation process. Proper HGMS content should be considered in the preparation process of three phase ESF.

(e) Some of the layers that seem very homogeneous and indeed is playing an important role in enhancing the compressive strength of the foam. The cellular structure developed in the matrix can give more lightweight structure in the foam, so the structure is also important in reducing the density of the foam. Therefore it needs to be taken into account as a void/cellular structure and its characterization is important as has a major impact in the final compressive strength and the density of the foam.

Acknowledgements

The work was supported by the Special Fund of the National Priority Basic Research of China (2014CB239503), the National Natural Science Foundation of China (51403124, 51303034), Project Funded by China Postdoctoral Science Foundation (2015M571459) and State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (LK1419).

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/
Glass fiber reinforced hollow epoxy macrospheres (GFR-HEMS) were prepared by “rolling ball method”. GFR-HEMS were embedded into a mixture of epoxy-hardener and 33.3 wt% HGMS to make three phase epoxy syntactic foam. Expanded polystyrene beads (EPS) were used as initiation template to prepare GFR-HEMS. The EPS beads were coated with the epoxy resin and glass fiber using “rolling ball method”, and these coated EPS beads were later cured and post-cured at high temperature which will shrink the EPS beads thus producing a hollow macrosphere structure.