Development and Mechanical Characterization of HGMS–EHS-Reinforced Hollow Glass Bead Composites

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ABSTRACT: Hollow glass microsphere-reinforced epoxy hollow spheres (HGMS–EHSs) were prepared by a “rolling ball method” using expanded polystyrene beads, HGMSs, and epoxy resin (EP). The three-phase epoxy syntactic foam (epoxy/HGMS–EHS–HGMS composite) was fabricated by combining HGMS–EHS as a lightweight filler with EP and HGMS by a “molding method.” The HGMS–EHS and epoxy curing agent systems were well mixed by scanning electron microscopy. Experiments show that higher HGMS–EHS layer number, higher HGMS–EHS diameter, lower HGMS–EHS density, higher HGMS volume fraction, and lower HGMS density result in a decrease in the density of the three-phase epoxy syntactic foam. However, the above factors have the opposite effect on the compressive strength of the three-phase epoxy syntactic foam. Therefore, in order to obtain the “high-strength and low-density” three-phase epoxy syntactic foam, the influence of various factors should be considered comprehensively to achieve the best balance of compressive strength and density of the three-phase epoxy syntactic foam. This can provide some advice for the preparation of buoyancy materials for deep sea operations.

INTRODUCTION

The solid buoyancy material is a low-density, high-strength, seawater-resistant composite foam material. It is mainly used to provide net buoyancy for various underwater operating systems, ensuring that its counterweight equipment can work stably and safely under water.1–3 At the same time, it also has the advantages of low water absorption, good weather resistance, resistance to hydrostatic pressure, and large safety and reliability. It can be applied to the buoy system, marine mining system, deep sea carrying operation equipment, marine survey and monitoring system, offshore oil system, and so forth.3–5 The syntactic foam buoyancy material forming process can be further subdivided into the casting method, the vacuum impregnation method, the liquid-transfer molding method, the particle deposition method, and the molding method.6 Among them, the compression molding method is ideal, and it is also the most commonly used molding method. In order to obtain a low-density solid buoyancy material, along with the addition of a blowing agent to the matrix resin, a lightweight filler may be added.6,7 The latter is the most effective way to obtain low-density three-phase composite buoyancy materials at present, among which the lightweight fillers are the most widely used hollow glass microspheres (HGMSs).5,9

HGMSs are hollow glass thin-walled beads with a diameter ranging from several micrometers to hundreds of micrometers and appear gray or white.10–13 It has many advantages such as loose drying, good fluidity, strong mechanical properties, low density, and so forth.14,15 The density of the HGMSs is generally in the range of 0.1–0.6 g/cm³, and the density of the three-phase composite buoyancy material prepared from the reinforced hollow spheres thereof is generally in the range of 0.2–0.7 g/cm³.16–18 Solid foam materials can be classified into one-phase foam materials and two-phase and three-phase syntactic foam materials because of their different compositions.19,20 The one-phase foam material mainly refers to a polymer-based foamed material such as a polystyrene foam material and a polyurethane foam material.21–24 The polymer foamed material has a low compressive strength and is highly limited. The two-phase syntactic foam material refers to a composite of epoxy resin (EP) and hollow glass microbeads, and the added HGMSs reduce the density of the buoyant material and show good compressive strength.25,26 The three-phase syntactic foam material is based on a two-phase syntactic foam material with some hollow materials, such as hollow glass bead-reinforced hollow spheres.27 Because the HGMS-reinforced hollow sphere has good compatibility with the resin matrix, it can be well combined in the preparation process.28 Therefore, the three-phase syntactic

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foam in which HGMS-reinforced hollow spheres are added not only has a lower density but also maintains a strong compressive strength.29,30

In this experiment, HGMS–epoxy hollow sphere (EHS) reinforced by hollow glass beads was used as the third phase to adjust the density of the three-phase epoxy syntactic foam. The three-phase epoxy syntactic foam was prepared by EP/HGMS-reinforced EHS (EP/HGMS–EHS/HGMS) by molding. The three-phase epoxy syntactic foam has the advantages of low density and high strength. The effects of HGMS–EHS diameter, stacking ratio, layers, types, and fillers on the density and compressive strength of the three-phase epoxy syntactic foam will be studied. The microstructures were analyzed by scanning electron microscopy (SEM).

■ RESULTS, ANALYSIS, AND DISCUSSION

HGMS–EHS Macroscopic Morphology and Density Characterization. Figure 1 shows the digital image of HGMS–EHS. As can be seen from the figure, the HGMS–EHS blended with the epoxy curing agent system/HGMS/EPS has a uniform surface. This feature facilitates better integration with the matrix, resulting in better mechanical properties of the three-phase composite buoyancy material.

Figure 2 shows the relationship between the HGMS–EHS diameter and density. Figure 2a is a representation of the density at different layers of HGMS–EHS with an initial diameter of 7–8 mm. As can be seen from the figure, the average density of the HGMS–EHS-1 layer is 0.092 g/cm³; the average density of the HGMS–EHS-3 layers is 0.249 g/cm³. Figure 2b is a representation of the density at different layers of HGMS–EHS with an initial diameter of 9–10 mm. As can be seen from the figure, the average density of the HGMS–EHS-1 layer is 0.079 g/cm³; the average density of the HGMS–EHS-3 layers is 0.221 g/cm³. Figure 2c shows the density characterization of HGMS–EHS with different types of HGMS. As can be seen from the figure, the average density of HGMS–EHS with K1 hollow glass microbeads was 0.103 g/cm³; the average density of HGMS–EHS with S38HS hollow glass microbeads was 0.158 g/cm³. Figure 2d is a comparison between the densities of two different diameters of HGMS–EHS. The average density of HGMS–EHS-2 layers-7–8 mm is 0.192 g/cm³; the average density of HGMS–EHS-2 layers-9–10 mm is 0.158 g/cm³.

It can be concluded from Figure 2a,b that when the initial diameter of the EPS is the same, the density of HGMS–EHS increases as the number of layers of HGMS–EHS increases. Figure 2c shows that the density of HGMS–EHS enhanced by S38HS is higher than that enhanced by K1 when the initial diameter of EPS is the same and all of them are 9–10 mm. It can be seen from Figure 2d that when the number of layers of HGMS–EHS is the same, the smaller the diameter of HGMS–EHS, the higher the density.

Characterization of Density and Compressive Strength of the Three-Phase Epoxy Syntactic Foam. Effect of HGMS–EHS Filled with Different Stacking Volume Ratios on Density and Compressive Strength of the Three-Phase Epoxy Syntactic Foam. Figure 3 is a graph showing the density change of a three-phase epoxy syntactic foam filled with different stacking volume fractions of HGMS–EHS. It can be seen from the figure that the density of the three-phase epoxy syntactic foam ranges from 0.578 g/cm³ (0%) to 0.575 g/cm³ (20%), 0.523 g/cm³ (40%), 0.487 g/cm³ (60%), 0.427 g/cm³ (80%), and 0.404 g/cm³ (90%). Figure 4 is a graph showing the compressive strength change of a three-phase epoxy syntactic foam filled with different stacking volume fractions of HGMS–EHS. It can be seen from the figure that the compressive strength of the three-phase epoxy syntactic foam ranges from 33.72 MPa (0%) to 29.96 MPa (20%), 27.05 MPa (40%), 22.08 MPa (60%), 19.76 MPa (80%), and 18.02 MPa (90%). From Figures 3 and 4, it can be concluded that the density and compressive strength of the three-phase epoxy syntactic foam without HGMS–EHS are the largest. With the increase of HGMS–EHS stacking volume fraction, the density and compressive strength begin to decrease. The three-phase epoxy syntactic foam without HGMS–EHS is actually a two-phase syntactic foam. It consists of an epoxy curing agent system and HGMSs. Its interior is solid and has no voids, so its compressive strength is very large. The compressive strength of the three-phase syntactic foam with HGMS–EHS (20, 40, 60, 80, 90%) begins to decrease. First, HGMS–EHS is the hollow material because it has already been shrunk inside itself. Second, the composite foam is no longer a pure entity, and voids have already been created. As the number of HGMS–EHS increases, the number of internal voids increases, and the compressive strength decreases.

From Figures 3 and 4, it can be concluded that with the increasing stacking volume fraction of HGMS–EHS, the density and compressive strength of the three-phase epoxy syntactic foam are reduced. Therefore, it is necessary to find the balance point between density and compressive strength so as to achieve the best combination of high strength and low density of the three-phase epoxy syntactic foam.

Characterization of Density and Compressive Strength of the Three-Phase Epoxy Syntactic Foam Filled with Different Layers of HGMS–EHS. Figure 5 is a graph showing the density change of the three-phase epoxy syntactic foam filled with different layers of HGMS–EHS at HGMS–EHS stacking volume fractions of 60, 80, and 90%. It can be seen from Figure 5a that the density of the three-phase epoxy syntactic foam ranges from 0.422 g/cm³ (0 layer) to 0.467 g/cm³ (1 layer), 0.487 g/cm³ (2 layers), and 0.510 g/cm³ (3 layers); the density of the three-phase epoxy syntactic foam in Figure 5b ranges from 0.367 g/cm³ (0 layer) to 0.409 g/cm³ (1 layer), 0.427 g/cm³ (2 layers), and 0.486 g/cm³ (3 layers); the density of the three-phase material in Figure 5c ranges from 0.317 g/cm³ (0 layer) to 0.380 g/cm³ (1 layer), 0.404 g/cm³ (2 layers), and 0.464 g/cm³ (3 layers). Figure 6 is a graph showing the compressive strength of the three-phase epoxy syntactic foam filled with different layers of HGMS–EHS at HGMS–EHS stacking volume fractions of 60, 80, and 90%. It can be seen
from Figure 6a that the compressive strength of the three-phase epoxy composite foam ranges from 10.54 MPa (0 layer) to 18.09 MPa (1 layer), 22.08 MPa (2 layers), and 27.42 MPa (3 layers); the compressive strength of the three-phase epoxy syntactic foam in Figure 6b ranges from 7.78 MPa (0 layer) to 15.41 MPa (1 layer), 19.76 MPa (2 layers), and 23.63 MPa (3 layers); and that shown in Figure 6c ranges from 7.08 MPa (0 layer) to 15.34 MPa (1 layer), 18.50 MPa (2 layers), and 23.58 MPa (3 layers). From the longitudinal view of Figures 5 and 6, that is, the density and compressive strength of the three-phase epoxy syntactic foam under four layers increase with the increase of HGMS−EHS volume fraction, which is consistent with the conclusion of Figures 3 and 4. With the increasing number of layers of HGMS−EHS, the compressive strength and density of the three-phase epoxy syntactic foam increase. Therefore, considering the density and compressive strength, HGMS−EHS (2 layers) is an ideal number of layers. The density compression ratios of the two-layer three-phase epoxy syntactic foam are:

Figure 2. Relationship between the HGMS−EHS diameter and density; (a) Ø EPS−7−8 mm (S38HS); (b) Ø EPS−9−10 mm (S38HS); (c) different HGMS, Ø EPS−9−10 mm; and (d) different diameter HGMS−EHS-2 layers.

Figure 3. Density of the three-phase epoxy syntactic foam filled with different stacking volume fractions of HGMS−EHS.

Figure 4. Compressive strength of the three-phase epoxy syntactic foam filled with different stacking volume fractions of HGMS−EHS.
0.0221 (60%), 0.0216 (80%), and 0.0218 (90%), respectively. By comparison, it can be concluded that the density compression ratio of the three-phase material filled with 80% HGMS–EHS is almost the same as that of the material filled with HGMS–EHS 90%, but the density of the three-phase material filled with 90% HGMS–EHS is lower. Therefore, it is desirable to choose HGMS–EHS volume fraction 90%.

Characterization of Density and Compressive Strength of the Three-Phase Epoxy Syntactic Foam Filled with Different Diameters of HGMS–EHS. Figure 7 is a graph showing the density change of a three-phase epoxy syntactic foam filled with different diameters of HGMS–EHS. It can be seen from the figure that the density of the three-phase epoxy syntactic foam ranges from 0.450 g/cm³ (the initial diameter of HGMS–EHS is 7–8 mm) to 0.404 g/cm³ (the initial diameter of HGMS–EHS is 9–10 mm). Figure 8 is a graph showing the change in compressive strength of a three-phase epoxy syntactic foam filled with different diameters of HGMS–EHS. From the figure, it can be concluded that the three-phase epoxy syntactic foam has a compressive strength of 22.50 MPa (the initial diameter of HGMS–EHS is 7–8 mm) to 18.02 MPa (the initial diameter of HGMS–EHS is 9–10 mm). It can be seen from Figures 7 and 8 that the density and compressive strength of the three-phase epoxy syntactic foam decrease with the increase of the diameter of HGMS–EHS.

Characterization of Density and Compressive Strength of the Three-Phase Epoxy Syntactic Foam Filled with Different Volume Fractions of HGMS (S38HS) in the Epoxy-Hardener System. Figure 9 is a graph showing the change in density of HGMS in the epoxy-hardener system of the three-phase epoxy syntactic foam. When the stacking volume fraction of HGMS–EHS in the mold is 90%, the density of the three-phase epoxy syntactic foam ranges from 0.492 g/cm³ (40%) to 0.453 g/cm³ (50%), 0.404 g/cm³ (60%), 0.367 g/cm³ (70%), and 0.342 g/cm³ (75%). Figure 10 is a graph showing the change in compressive strength of HGMS in the epoxy-hardener system of a three-phase epoxy syntactic foam. It can be seen from the figure that the compressive strength of the three-phase epoxy syntactic foam ranges from 14.10 MPa (40%) to 16.07 MPa (50%), 18.02 MPa (60%), 18.70 MPa (70%), and 17.03 MPa (75%). Figure 11 shows the digital image of the three-phase epoxy syntactic foam filled with different volume fractions of HGMS (S38HS) in the epoxy-hardener system. As can be seen from the figure, there is no HGMS–EHS in the lower half of the sample (40%); there are some HGMS–EHS in the lower half of the sample (50%); in samples filled with HGMS (60%), HGMS–EHS was distributed throughout the three-phase foam. Referring to Figures 9 and 10, it can be concluded that the density of the three-phase epoxy syntactic foam decreases as the volume fraction of HGMS increases, and the compressive strength of the three-phase epoxy syntactic foam increases first and then decreases because the HGMS/epoxy curing agent system mixes well when the HGMS volume fraction is low. When HGMS–EHS was added, the volume fraction of HGMS–EHS continued to rise because of the fluidity of the substrate. However, HGMS–EHS in the lower half of the three-phase epoxy syntactic foam becomes very less, that is, HGMS–EHS is unevenly distributed in the entire three-phase epoxy syntactic foam, and the compression strength is low. As the volume fraction of HGMS increases, the fluidity of the HGMS/epoxy curing agent system becomes poor. The degree of floating of HGMS–EHS becomes less, that is, it is evenly distributed throughout the three-phase epoxy syntactic foam. Because HGMS–EHS is concentrated in the upper part, the direct contact probability between HGMS–EHS and HGMS–EHS is increased, and the compressive strength of the three-phase
epoxy composite foam is lower. It can be seen from the figure that when the volume fraction of HGMS is 70%, the compressive strength of the three-phase epoxy syntactic foam reaches the maximum (18.07 MPa). When the volume fraction of HGMS reaches 75%, the compressive strength of the three-phase epoxy syntactic foam begins to decrease. The reason is that when 75% of HGMS is filled into the epoxy curing agent system, the entire substrate is almost free of fluidity, resulting in some HGMS−EHS and HGMS−EHS being in direct contact with each other. The anticompression ability of HGMS−EHS itself is very poor, and it can be seen from Figure 3 that the pure matrix has a strong anticompression ability. It is precisely due to the adhesion of the matrix that all of HGMS−EHS are combined to make the compression resistance of HGMS−EHS stronger. Without the bonding of the matrix, the compression resistance of HGMS−EHS becomes poor, resulting in a decrease in the compressive strength of the entire three-phase epoxy syntactic foam. Characterization of Density and Compressive Strength of the Three-Phase Epoxy Composite Foam Filled with Different Kinds of HGMS−EHS. Figure 12 is a graph showing the change in density of a three-phase epoxy composite foam filled with different types of HGMS−EHS.
can be seen from the figure that the density of the three-phase epoxy composite foam to which HGMS–EHS (K1) is added is 0.331 g/cm³; the density of the three-phase epoxy composite foam with HGMS–EHS (S38HS) is 0.404 g/cm³. Figure 13 is a graph showing the change in compressive strength of a three-phase epoxy composite filled with different types of HGMS–EHS. It can be seen from the figure that the maximum compressive strength of the three-phase epoxy composite foam with HGMS–EHS (K1) is 16.05 MPa; the maximum compressive strength of the three-phase epoxy composite foam with HGMS–EHS (S38HS) is 18.02 MPa. From the above two figures, it can be concluded that as the density of the HGMSs increases, the density and compressive strength of the three-phase epoxy composite foam increase.

**Characterization of Density and Compressive Strength of the Three-Phase Syntactic Foam Filled with Different HGMS-Enhanced Fillers.** Figure 14 is a graph showing the change in density of a three-phase epoxy composite foam filled with different volume fractions of HGMS (S38HS) in the epoxy-hardener system.
syntactic foam filled with different HGMS-enhanced fillers. It can be seen from the figure that the density of the three-phase epoxy syntactic foam filled with HGMS (K1) is 0.347 g/cm$^3$; the density of the three-phase epoxy syntactic foam filled with HGMS (S32) is 0.376 g/cm$^3$; and the density of the three-phase epoxy syntactic foam filled with HGMS (S38HS) is 0.404 g/cm$^3$. Figure 15 is a graph showing the change in compressive strength of the three-phase epoxy syntactic foam.

Figure 15. Compressive strength of the three-phase epoxy syntactic foam filled with different HGMS-reinforced fillers.

For the three sets of comparisons, the same HGMS–EHS was used, including the initial diameter, volume fraction, type, number of layers of HGMS–EHS, and the volume fraction of HGMS in the epoxy curing agent system. The difference is that there are only different types of HGMS in the filler. Among the three HGMSs, the K1 density is the lowest, S32 is the second, and S38HS is the highest. Therefore, from Figures 14 and 15, it can be concluded that as the density of HGMS in the filler increases, the density and compressive strength of the three-phase epoxy syntactic foam increase.

**Morphological Characterization of the Three-Phase Epoxy Syntactic Foam.** Figure 16 shows the sectional view of the three-phase epoxy syntactic foam. The general structure of the three-phase epoxy composite foam can be seen from the cross-sectional view, where a represents an epoxy curing agent system–hollow glass microbead composite two-phase system (epoxy/hardener-HGMS), b represents an EHS (HGMS–EHS), c/d is the contracted EPS sphere in HGMS–EHS, and e/f are hole defects. It can be seen from the figure that the centimeter-element EHS (HGMS–EHS) is evenly dispersed in the epoxy/hardener-HGMS, and the EPS template has also been uniformly shrunk in HGMS–EHS. This shows that the composite produced is still very uniform. It can also be found that there is no obvious interface between HGMS–EHS and epoxy/hardener-HGMS and they are very tightly combined. The main reason is due to the fact that the EP for preparing the centimeter hollow sphere HGMS–EHS is the same as the EP in epoxy/hardener-HGMS, so the interface is tightly combined. The holes e and f are produced because of the ingress of air during mixing and preparation. The pores increase the porosity of the three-phase material, which leads to a decrease in the bonding strength of the material and also adjusts the overall density and performance of the material.

Figure 16. Sectional view of the three-phase epoxy syntactic foam.

Figure 17 is an SEM image of the three-phase epoxy syntactic foam. The figure is divided into three parts a, b, and c; a is the inner surface of the sphere; b is the wall of the sphere; c is the outer surface of the sphere, and inside the red circle is HGMS. It can be seen from the figure that the inner surface of the sphere is relatively smooth, which helps to improve the performance of HGMS–EHS and the three-phase epoxy syntactic foam. The dispersion of HGMS in the sphere wall and the outer surface of the sphere is relatively uniform, and the bonding between HGMS and HGMS connected by the epoxy curing agent is also very tight, which is beneficial to the performance of three-phase materials. At the same time, it can be seen from the figure that there is no obvious boundary between the sphere wall and the outer surface of the sphere because the composition of both HGMS and EP is the same. Because of the same material used, the bond between HGMS–EHS and the epoxy curing agent system is better and less prone to breakage.

**CONCLUSIONS**

1. The influence of stacking volume fraction of HGMS–EHS: the maximum compressive strength [HGMS (S38HS), 60%] of the three-phase epoxy syntactic foam decreases with the increasing stacking volume fraction of HGMS–EHS (9–10 mm, 2 layers) from 33.72 MPa (0%) to 29.96 MPa (20%), 27.05 MPa (40%), 22.08 MPa (60%), 19.76 MPa (80%), and 18.02 MPa (90%). Its density also decreases as the HGMS–EHS stack volume
Table 1. Formulation of the Experimental Material

| material name | specification or purity | material origin |
|---------------|-------------------------|-----------------|
| EP (EPOLAM2070) | Amber, the Brookfield viscosity is 2800 mPa·s at 25 °C and the density is 1.17 g/cm³ at 25 °C | AXSON Technologies Shanghai Co. Ltd., China |
| hardener | dark Amber, the Brookfield viscosity is 13 mPa·s at 25 °C and the density is 0.92 g/cm³ at 25 °C | AXSON Technologies Shanghai Co. Ltd., China |
| HGMSs (S38HS) | white, the compressive strength is 37.90 MPa, the true density is 0.38 g/cm³, and the particle size is 15–85 μm | Minnesota Mining and Manufacturing, Shanghai, America |
| HGMSs (S32) | white, the compressive strength is 13.78 MPa, the true density is 0.32 g/cm³, and the particle size is 20–80 μm | Minnesota Mining and Manufacturing, Shanghai, America |
| HGMSs (K1) | white, the compressive strength is 1.72 MPa, the true density is 0.15 g/cm³, and the particle size is 30–120 μm | Hangzhou Hangchao Packaging Materials Co. Ltd., China |
| EPS foam ball foam particles | the density is 10 kg/m³ | |

fraction increases from 0.578 g/cm³ (0%) to 0.575 g/cm³ (20%), 0.523 g/cm³ (40%), 0.487 g/cm³ (60%), 0.427 g/cm³ (80%), and 0.404 g/cm³ (90%).

2 The influence of layers of HGMS–EHS: when the stacking volume fraction of HGMS–EHS is 90%, the compressive strength of the three-phase syntactic foam increases from 7.08 MPa (0 layer) to 15.34 MPa (1 layer), 18.50 MPa (2 layers), and 23.58 MPa (3 layers). The compressive strength of the three-phase epoxy composite foam increases with the increase of the HGMS–EHS layer. With the increasing number of layers of HGMS–EHS, the compressive strength and density will increase. Because the three-phase epoxy composite foam prepared by HGMS–EHS (2 layers) has higher compressive strength than HGMS–EHS (1 layer), the density is not as large as that produced by HGMS–EHS (3 layers). In order to balance the density and compressive strength of the three-phase foam, the two-layer HGMS–EHS is ideal.

3 The influence of diameter of HGMS–EHS: the larger the diameter of the EPS template, the larger the diameter of the produced HGMS–EHS. The compressive strength of the three-phase epoxy syntactic foam was reduced from 22.50 MPa (HEMS-EHS-7–8 mm 2 layers) to 18.02 MPa (HEMS-EHS-9–10 mm 2 layers). When the large-diameter HGMS–EHS-filled three-phase epoxy syntactic foam has a lower density, its compression strength also decreases. Therefore, the diameter of the EPS should be selected according to actual needs.

4 The influence of density of HGMS–EHS: when the stacking volume fraction of HGMS–EHS is 90%, the compressive strength of the three-phase epoxy syntactic foam from 16.05 MPa (HGMS–EHS-K1–9–10 mm 2 layers) to 18.02 MPa (HGMS–EHS-S38HS-9–10 mm 2 layers). Therefore, it can be concluded that the compressive strength of the three-phase epoxy syntactic foam increases as the density of HGMS–EHS increases. When the density of the three-phase epoxy syntactic foam filled with HGMS–EHS (S38HS) becomes higher than that of HGMS–EHS (K1), the compressive strength also increases. Therefore, it is necessary to select a specific type of HGMS–EHS according to specific requirements.

5 The influence of volume fraction of HGMS: the compressive strength of the three-phase epoxy syntactic foam increases from 14.10 MPa (40%) to 16.07 MPa (50%), 18.02 MPa (60%), and 18.70 MPa (70%) and then decreases down to 17.03 MPa (75%). The compressive strength of the three-phase epoxy syntactic foam increases from 40 to 70%. The reason is that with the increasing HGMS volume fraction, the fluidity of the matrix is getting worse and worse, resulting in the decrease of HGMS–EHS flotation, that is, HGMS–EHS can be distributed evenly throughout the three-phase epoxy syntactic foam. When the volume fraction of HGMS reaches 75%, the compressive strength of the three-phase epoxy syntactic foam suddenly drops. The reason is that the matrix filled with HGMS (75%) has substantially no fluidity, which makes it easy for HGMS–EHS to come in contact with each other so that the entire foam has poor compression strength.

6 The influence of HGMS type: when the HGMS in the epoxy curing agent/HGMS system has the same volume fraction (60%), the compressive strength of the three-phase epoxy syntactic foam reduces from 18.02 MPa (S38HS) to 17.40 MPa (S32) and 9.03 MPa (K1). Because the density of different HGMSs is different, the densities of the three HGMSs of K1, S32, and S38HS are 0.125, 0.32, and 0.38 g/cm³, respectively. When the density of HGMS increases, the density and strength of HGMS–EHS will increase first, and then the density and compressive strength of the three-phase epoxy syntactic foam, which is composed of HGMS–EHS as a filler, will also increase. From the above discussion, it can be concluded that the type of HGMS will affect the density of the three-phase epoxy syntactic foam, but the effect on its compressive strength is the opposite. Therefore, in order to obtain a higher strength three-phase epoxy syntactic foam, HGMS (S38HS) or HGMS (S32) can be selected. In order to pursue the low-density performance of the three-phase epoxy syntactic foam, HGMS (K1) can be selected. In practice, the type of HGMS should be selected according to the requirements of working conditions (Table 1).

**EXPERIMENTAL SECTION**

**Materials. Experimental Formula.** In order to compare the effects of different diameters, different layers, different types, different volume fractions of HGMS–EHS, different volume fractions of HGMS, and different epoxy curing agent systems on the performance of the three-phase epoxy syntactic foam, in this experiment the following ratios were adopted. The initial foam balls (EPS) were 7–8, 9–10 mm. The number of layers of HGMS–EHS was 1, 2, 3 layers. Hollow glass bead-enhanced hollow spheres: K1 enhancement hollow spheres and S38HS enhanced hollow spheres. Three HGMSs are set in the matrix: S38HS, S32, and K1 (see Table 2 for details).

**Preparation of the Epoxy Composite-Reinforced Hollow Sphere.** HGMS–EHS was prepared by a "rolling
Figure 18. Preparation process of HGMS–EHS. (a) EPS. (b) Epoxy system-coated EPS. (c) Epoxy system/HGMS-coated EPS. (d) HGMS–EHS.

and an HGMS, that is, an unreduced core HGMS–EHS and (d) is the HGMS–EHS after heat shrinking.

The preparation process is as follows: step 1: 3 parts of EP and 1 part of curing agent are weighed and placed in a defoaming mixer, and the stirring time is set to 5 min, the rotation speed is 2000 rpm, and then the epoxy curing agent system can be obtained. Step 2: weigh a certain amount of EPS (Figure 18a) and the epoxy curing agent system to mix evenly. (The ratio of epoxy curing agent to EPS ball is 39 g of EP and 13 g of curing agent per 10 g of pellets). Step 3: put the epoxy system-coated EPS (Figure 18b) into the ball machine and add HGMS. After the ball is evenly distributed, remove the epoxy system/HGMS-coated EPS (Figure 18c). Finally, the epoxy system/HGMS-coated EPS was heated in a vacuum drying oven (DZF, Shanghai Yiheng Instruments Co., Ltd., China) at 50 °C for 2 h, and the internal EPS pellets were denucleated. After cooling, the HGMS–EHS was obtained (Figure 18d). Figure 1 shows the preparation process of one-layer HGMS–EHS, and the two-layer HGMS–EHS performs the process of Figure 1 on the basis of 1 layer and so forth.

Preparation of the Three-Phase Epoxy Syntactic Foam.

Figure 19 shows the preparation process of the three-phase epoxy syntactic foam. Step 1: configure the filler, that is, place the EP, curing agent, and HGMS in a stirred container and then mix well. The proportion of EP and curing agent is 3:1 (Figure 19a). Step 2: this step is based on the volume of the entire mold (Ø 70 mm × 65 mm, H 60 mm). HGMS–EHS was completely filled into the mold (100%), and then HGMS–EHS with different stacking volume fractions was selected according to the experimental ratio. Step 3: fill the filler with HGMS–EHS into the mold. It is necessary to wipe the inside of the mold and the polyester film multiple times with a release agent before filling in order to prepare the prepared sample to be flat and easy to remove from the mold. Step 4: pressurize with a hot and cold press (CS-105H, Huizhou Chengsheng Hardware Machinery Equipment Co., Ltd., China) (Figure 19b). A constant load of a standard weight (5.0 kg/cm²) was placed on top of the mold to keep the HGMS–EHS fully dispersed and prevented from floating. First, pressurize with a hot press at a temperature of 100 °C for 1 h and then pressurize with a cold press for 15 min. Step 5: the three-phase composite foam was allowed to stand at room temperature for 48 h to complete the curing process (Figure 19c). The quality of each component is calculated as follows

$$M_{HGMS} = V_{mold} \times (1 - V_{HGMS-EHS}) \times 1.12 \text{ g/cm}^3 \times 60\%$$
Table 3. Formulation of the Three-Phase Epoxy Syntactic Foam Filled with Different Stacking Volume Fractions of HGMS—EHS

| influence factor | sample 1 | sample 2 | sample 3 | sample 4 | sample 5 | sample 6 |
|------------------|----------|----------|----------|----------|----------|----------|
| stacking volume fraction of HGMS—EHS (%) | 60 | 60 | 60 | 60 | 60 | 60 |
| initial diameter of HGMS—EHS (mm) | 9–10 | 9–10 | 9–10 | 9–10 | 9–10 | 9–10 |
| wall thickness layer of HGMS—EHS | 2 layers | 2 layers | 2 layers | 2 layers | 2 layers | 2 layers |
| the proportion of HGMS in the epoxy curing agent/HGMS system (%) | 60 | 60 | 60 | 60 | 60 | 60 |
| type of HGMS in the epoxy curing agent/HGMS system | S38HS | S38HS | S38HS | S38HS | S38HS | S38HS |

Table 4. Formulation of the Three-Phase Epoxy Syntactic Foam Filled with Different Layers of HGMS—EHS at 60, 80, and 90% Stacking Volume Fractions

| influence factor | sample 1 | sample 2 | sample 3 | sample 4 |
|------------------|----------|----------|----------|----------|
| stacking volume fraction of HGMS—EHS (%) | 80 | 80 | 80 | 80 |
| initial diameter of HGMS—EHS (mm) | 9–10 | 9–10 | 9–10 | 9–10 |
| wall thickness layer of HGMS—EHS | 0 layer | 1 layer | 2 layers | 3 layers |
| the proportion of HGMS in the epoxy curing agent/HGMS system | 60 | 60 | 60 | 60 |
| type of HGMS in the epoxy curing agent/HGMS system | S38HS | S38HS | S38HS | S38HS |

Table 5. Formulation of the Three-Phase Epoxy Syntactic Foam Filled with Different Diameters of HGMS—EHS

| influence factor | sample 1 | sample 2 |
|------------------|----------|----------|
| stacking volume fraction of HGMS—EHS (%) | 90 | 90 |
| initial diameter of HGMS—EHS (mm) | 9–10 | 9–10 |
| wall thickness layer of HGMS—EHS | 0 layer | 1 layer |
| the proportion of HGMS in the epoxy curing agent/HGMS system | 60 | 60 |
| type of HGMS in the epoxy curing agent/HGMS system | S38HS | S38HS |

Preparation of the Three-Phase Epoxy Syntactic Foam Filled with Different Bulk Volume Fractions of HGMS—EHS. Table 3 shows the formulation of the three-phase epoxy syntactic foam filled with different bulk volume fractions of HGMS—EHS. In order to study the effect of HGMS—EHS with different stacking volume fractions on the compressive strength of the three-phase epoxy syntactic foam, six groups of HGMS—EHS (S38HS) with different stacking volume fractions of 0, 20, 40, 60, 80, and 90% were selected as fillers to be added into the three-phase epoxy syntactic foam. The HGMS—EHS (0%) group was used as a blank compared to the other five groups. The variable for this experiment is the stacking volume fraction of HGMS—EHS (S38HS) in the three-phase epoxy syntactic foam.

Preparation of the Three-Phase Epoxy Syntactic Foam Filled with Different Layers of HGMS—EHS. Table 4 shows the formulations of the three-phase epoxy composite foam filled with different layers of HGMS—EHS (S38HS) under the HGMS—EHS 60, 80, and 90% cumulative volume fractions, respectively. When the initial diameters of HGMS—EHS were the same, in order to study the effect of different layers of HGMS—EHS (S38HS) on the mechanical properties of the three-phase composite foam, different layers of HGMS—EHS were added to the two-phase composite foam. There are two variables in this experiment: one is the volume fraction of different HGMS—EHSs (60, 80, 90%) and the other is the number of layers of HGMS—EHS (0 layer, 1 layer, 2 layers, 3 layers).

Preparation of the Three-Phase Epoxy Syntactic Foam Filled with Different Diameters of HGMS—EHS. Table 5 shows the formulation of the three-phase epoxy syntactic foam filled with different diameters of HGMS—EHS. HGMS—EHS (S38HS) with different initial diameters also affects the mechanical properties of the three-phase epoxy syntactic foam. GR-HEMS with different inner diameters (7–9, 9–10 mm) was added into the two phase composite to make three-phase ESF, respectively. The variable for this experiment is the diameter of the HGMS—EHS.
Preparation of the Three-Phase Epoxy Syntactic Foam Filled with Different Volume Fractions of HGMS (S38HS) in the Epoxy-Hardener System. Table 7 shows the formulation of the three-phase epoxy syntactic foam filled with different volume fractions of HGMS (S38HS). In order to study the effect of different volume fractions of HGMS (S38HS) on the compressive strength of the three-phase epoxy composite foam, HGMS with different volume fractions (40, 50, 60, 70, and 75%) was added into the epoxy-hardener system to make the two-phase composite foam, respectively. Then, 90% stacking volume fraction of HGMS—EHS was added into the two-phase composite foam to make the three-phase epoxy syntactic foam.

Preparation of the Three-Phase Epoxy Syntactic Foam Filled with Different HGMS-reinforced Fillers. Table 8 shows the formulation of the three-phase epoxy syntactic foam filled with different hollow glass microbead-reinforced fillers. In order to investigate the effect of different types of fillers on the compressive strength of the three-phase epoxy syntactic foam, HGMS—EHS (S38HS) with a 90% stacking volume fraction was added as a filler to the syntactic foam. The variable for this experiment was the filler. Three different hollow glass beads of S38HS, S32, and K1 were selected for the preparation of the filler to be mixed with the epoxy-hardener system.

Performance Measurement and Characterization. The calculation of HGMS—EHS density is based on the random selection of HGMS—EHS. The purpose of random selection is to avoid the contingency of the experiment. Fifty samples were selected for each diameter and type. The diameter and mass of 50 samples were measured using a digital vernier caliper (SHAHE, Ningbo KECHENG Instrument Co., Ltd., China) (accuracy of 0.01 mm) and a digital analytical balance (FA1106, Biuged Laboratory Instruments (Guangzhou) Co., Ltd., China) (accuracy of 0.001 g). The average density of HGMS—EHS was calculated using the total mass of 50 samples versus the total volume of the top 50 samples. The formula is as follows:

$$\rho_{\text{HGMS–EHS}} = \frac{\sum_{i=1}^{50} M_{\text{HGMS–EHS}}}{\sum_{i=1}^{50} V_{\text{HGMS–EHS}}}$$

Table 7. Formulation of the Three-Phase Epoxy Syntactic Foam Filled with Different Volume Fractions of HGMS (S38HS) in the Epoxy-Hardener System

| influence factor | sample 1 | sample 2 | sample 3 | sample 4 | sample 5 |
|------------------|----------|----------|----------|----------|----------|
| stacking volume fraction of HGMS—EHS (%) | 90 | 90 | 90 | 90 | 90 |
| initial diameter of HGMS—EHS (mm) | 9–10 | 9–10 | 9–10 | 9–10 | 9–10 |
| wall thickness layer of HGMS—EHS | 2 layers | 2 layers | 2 layers | 2 layers | 2 layers |
| volume fraction of HGMS in the epoxy curing agent/HGMS system (%) | 40 | 50 | 60 | 70 | 75 |
| type of HGMS in the epoxy curing agent/HGMS system | S38HS | S38HS | S38HS | S38HS | S38HS |

Table 8. Formulation of the Three-Phase Epoxy Syntactic Foam Filled with Different HGMS-Reinforced Fillers

| influence factor | sample 1 | sample 2 | sample 3 | sample 4 | sample 5 |
|------------------|----------|----------|----------|----------|----------|
| stacking volume fraction of HGMS—EHS (%) | 90 | 90 | 90 | 90 | 90 |
| initial diameter of HGMS—EHS (mm) | 9–10 | 9–10 | 9–10 | 9–10 | 9–10 |
| wall thickness layer of HGMS—EHS | 2 layers | 2 layers | 2 layers | 2 layers | 2 layers |
| the proportion of HGMS in the epoxy curing agent/HGMS system (%) | 60 | 60 | 60 | 60 | 60 |
| type of HGMS in the epoxy curing agent/HGMS system | S38HS | S38HS | S38HS | S38HS | S38HS |

Three-phase composite buoyancy material density calculation: for a three-phase composite buoyancy material, the mass is measured with a digital analytical balance (accuracy of 0.001 g). The volume is the volume of the mold (Ø 70 mm × 65 mm, H 60 mm), and the density is the mass divided by the volume.

The mechanical properties of the three-phase composite buoyancy material samples were tested by an electronic universal testing machine (CMT5350, Shenzhen Suns Technology Co., Ltd., China). This experiment used GB/T16491-2008 as the standard.

SEM (JEM-4701, JEOL, Japan) was used to observe the wall thickness of the HGMS-enhanced sphere and its microscopic morphology with the bond site of the epoxy curing agent system. Before SEM observation, the sample should be cleaned by an ultrasonic cleaner (SK2200H, Shanghai Kudos Ultrasonic Instrument Co., Ltd., China) in order to remove some dust and make the observation results clearer. The principle of preparation of the SEM sample is as follows: as far as possible, the position where the ball is relatively regular or large is selected. The sample includes epoxy curing agent/HGMS system and HGMS—EHS. The sample used is thin, so it needs to be sprayed with gold in order to impart it strong conductivity and to make the observation results clearer.

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Notes
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