Preparation and Mechanical Properties of Carbon Fiber Reinforced Multiphase Epoxy Syntactic Foam (CF-R-Epoxy/HGMS/CFR-HEMS Foam)

Xinfeng Wu,† Yuan Gao,† Ying Wang, Tao Jiang, Jinhong Yu,*, Ke Yang, Yuantao Zhao,*, and Wenge Li*

ABSTRACT: Short carbon fiber (CF), epoxy-hardener (EP-hardener), and expanded polystyrene (EPS) beads were used to prepare CF-reinforced hollow epoxy macrospheres (CFR-HEMS) by the "rolling ball method". The multiphase epoxy syntactic foam (ESF) was prepared with CFR-HEMS, the EP-hardener system, and hollow glass microspheres (HGMS) by the "compression modeling method". In this experiment, the influences of the stacking volume fraction, wall thickness, and inner diameter of the CFR-HEMS and HGMS types and contents in the EP-hardener system on the properties of the ESF were studied. In addition, CFs with different meshes were used to reinforce hollow epoxy macrospheres (HEMS) to study the effect of different kinds of CFs on the compressive strength of the ESF. During the mixing of the EP-hardener and HGMS (EP-hardener−HGMS), 300 AW CFs with different contents were added to the system to enhance the compressive strength of the ESF. The CFR-HEMS spherical wall was combined tightly with the EP-hardener−HGMS system by a scanning electron microscope (SEM). The ESF, which has better properties relatively in the experiment, can be used in 2673 m deep water and provide 490 kg/m³ buoyancy, which can be of help in the preparation of buoyancy materials in detection systems and oil extraction systems in the deep sea.

INTRODUCTION

Epoxy syntactic foams (ESFs) are used in the manufacture of automobiles, aerospace, marine buoyancy blocks, and diving equipment on a large scale as low-density materials with high compressive strength.1,2 In particular, ESF materials are widely used in oil and gas mining pipelines and in underwater unmanned vehicles.3,4 In the sea, the deeper the water is, the more pressure the equipment should be able to withstand. However, ESFs not only need to withstand huge deepwater pressure but also provide sufficient buoyancy.5,6 Buoyancy materials with better compressive strength and lower density are used more widely in the deep-sea environment.7

Foams made from different raw materials can be divided into one-phase, two-phase, and multiphase foam materials.8–10 One-phase foam is mainly polymer foam. This kind of foam is prepared by the "chemical foaming method" to obtain low-density foam. One-phase foam can easily absorb water when immersed in water and cannot be used for a long time.11 Although this kind of foam has a low density (0.2 g/cm³), it can only be applied in the shallow sea because of its poor compressive strength.12–18 Two-phase foam materials are mainly prepared by combining hollow microspheres with the EP-hardener system.19–21 Due to the high density of the EP-hardener system, the density of two-phase foam (0.6–0.9 g/cm³) is larger than that of one-phase foam materials. The main purpose of adding hollow microspheres is to reduce the density of two-phase foam. Hollow microspheres are mostly made of ceramic, polymer, and glass materials.22–29 The unique hollow spherical structure of hollow microspheres facilitates force transmission. Compared with other types of hollow microspheres, hollow glass microspheres (HGMS) have excellent properties of high compressive strength and low density. HGMS have been the core material in buoyancy materials applied...
widely in the deep-sea environment. The addition of HGMS could improve the compressive strength of two-phase foam and reduce the density greatly, but it is unrealistic to rely on too much HGMS to reduce the density of two-phase foam. The volume fraction of HGMS that could be filled into the EP-hardener system is in the range of 0−70%. The addition of too much HGMS will make the viscosity of the EP-hardener−HGMS system too high. Many air bubbles will be formed during the curing process, causing a reduction in the compressive strength of two-phase foam. Due to the limitation of the addition of HGMS, the density of two-phase foam is rarely lower than 0.6 g/cm³. The addition of hollow epoxy macrospheres (HEMS) could further reduce the density of ESF, but the choice of reinforcing materials for HEMS is important. Previously, CF, HGMS, and calcium carbonate (CaCO₃) were used as coating materials for reinforcing HEMS. The density of CaCO₃ powder is large (2.5 g/cm³), which limits the buoyancy that ESF can provide. SS Samsun used CaCO₃-reinforced HEMS to prepare multiphase foam with the density of 0.57 g/cm³ and the compressive strength of 19.76 MPa. It can be seen that CaCO₃ powder is not the best choice to enhance the performance of HEMS. The density of CF (1.76 g/cm³) is lower than that of CaCO₃ powder. The CF as a one-dimensional material can easily form a guiding structure inside composite materials, which is conducive to improve the overall compressive strength of the ESF. In the experiment, HEMS were reinforced with CF by the “rolling ball method” and the ESF was prepared by the “pouring method” and the “compression modeling method”. Because of the simple preparation process, the pouring method is widely used in laboratory preparation of ESF. However, the EP-hardener−HGMS system has a certain viscosity, and air bubbles are easily formed during the pouring process. These bubbles weaken the compressive strength of the ESF but are beneficial to reduce the density of the ESF.

In the experiment, ESFs with different components were prepared by changing the stacking volume fraction, layer, and inner diameter of the CFR-HMES, and three kinds of HGMS were used to prepare ESFs. CFs with different meshes were used to reinforce the HEMS to study the effect of different kinds of CFs on the compressive strength of ESFs. CFs of 300 AW with different contents were innovatively added to the system, hoping that combining CFR-HEMS, HGMS, and CF can further improve the overall compressive strength of ESFs.

■ RESULTS AND DISCUSSION

Physical Property of CFR-HEMS. Figure 1 shows nine kinds of CFR-HEMS with different inner diameters and layers. CFR-HEMS have a regular shape and smooth surface. The smooth surface greatly improves the binding ability of the matrix with CFR-HEMS, which has a great impact on the compressive strength of CFR-HEMS. The physical properties of ESF are also different due to the different inner diameters and layers of CFR-HEMS.

Figure 2 shows the relationships between the diameter and density of 11 kinds of CFR-HEMS. Obviously, with the layers of CFR-HEMS increased, the quality and strength of CFR-HEMS increased significantly. According to Figure 2a−c, it can be seen that the more the layers of CFR-HEMS, the larger is the wall thickness, which is beneficial to improving the compressive strength of CFR-HEMS and also ESF, but not conducive to reduce the density of ESF. The buoyancy of ESF is limited. According to the performance of ESF required for different marine environments, a suitable wall thickness must be selected.

The relationship between its compressive strength and density should be balanced. From the data of 60 groups of CFR-HEMS with 9−10 mm inner diameters and different layers, it can be seen that the CFR-HEMS in Figure 2a are divided into the following three regions:

(1) CFR-HEMS-1 layer, 0.12−0.21 g/cm³ (diameter 9.2−10.3 mm);
(2) CFR-HEMS-2 layers, 0.25−0.37 g/cm³ (diameter 9.8−11.0 mm); and
(3) CFR-HEMS-3 layers, 0.43−0.58 g/cm³ (diameter 10.8−11.6 mm).

From the data, it can be seen that because the inner diameters of the CFR-HEMS are not the same, the particle sizes and the density of the CFR-HEMS keep changing. For CFR-HEMS, the inner diameter is 9−10 mm, and the average densities are calculated to be 0.159 g/cm³ (1 layer), 0.318 g/cm³ (2 layers), and 0.483 g/cm³ (3 layers). From the calculated data, it can be obtained that the average density of CFR-HEMS increases with the layers increasing. The average density of CFR-HEMS can be calculated by formula (1)

\[
\rho_{CFR-HEMS} = \frac{\sum_{n=0}^{60} (m_n)_{CFR-HEMS}}{\sum_{n=0}^{60} (V_n)_{CFR-HEMS}}
\]

When the inner diameters of CFR-HEMS are 7−8 and 11−12 mm, the regulation of the density is roughly the same as when the inner diameter of CFR-HEMS is 9−10 mm. According to Figure 2a, when the inner diameter is 7−8 mm, the average densities are 0.190 g/cm³ (1 layer), 0.345 g/cm³ (2 layers), and 0.492 g/cm³ (3 layers). According to Figure 2c, when the diameter is 11−12 mm, the average densities are 0.155 g/cm³ (1 layer), 0.327 g/cm³ (2 layers), and 0.466 g/cm³ (3 layers).

When the CFR-HEMS have different inner diameters and the same layers, as shown in Figure 2d, 180 samples of CFR-HEMS having inner diameters of 7−8, 9−10, and 11−12 mm are used. The data is evenly distributed in the three areas. When the inner diameter is the smallest (7−8 mm), the density of CFR-HEMS is the largest. The average densities of CFR-HEMS significantly decrease with the inner diameters increasing. The average density of CFR-HEMS with inner diameter 9−10 mm is reduced by about 8.56% compared to CFR-HEMS with inner diameter 7−8 mm. The average density of CFR-HEMS with inner diameter 11−12 mm is only reduced by about 0.22% compared to CFR-HEMS with inner diameter 9−10 mm, which also provides a relevant basis for reducing the density of ESFs.

Figure 1. Nine kinds of CFR-HEMS with different inner diameters and layers.
In addition, 30 AW, 100 AW, and 300 AW CFs were used in the experiment to prepare two layers of CFR-HEMS with inner diameter 9–10 mm. It can be seen from Figure 2e that although three distribution areas have overlapping areas, the average density of CFR-HEMS increases with the mesh size increasing. The average densities of three kinds of CFR-HEMS were 0.195
g/cm³ (30 AW), 0.246 g/cm³ (100 AW), and 0.318 g/cm³ (300 AW).

Although reducing the density of CFR-HEMS is beneficial to reduce the density of ESFs, the compressive strength of ESFs will be affected. In the following sections, ESFs made from different CFR-HEMS systems will be studied.

Physical Property of ESFs. By observing the macropicture inside the ESF in Figure 3, the structure of the ESF can be seen clearly, and the expanded polystyrene (EPS) beads shrank under a high-temperature environment. It can be seen from the yellow marks in Figure 3 that the diameters of the shrinkable EPS beads are only 1/4 times that of the original EPS beads, and the shrinkable EPS beads were attached to the inner wall of CFR-HEMS. From the red marks in Figure 3, the inner wall of CFR-HEMS is smooth and regular to be a round shape. The wall is tightly combined with the EP-hardener–HGMS system, which improves the compressive strength of ESFs. The addition of CFR-HEMS reduces the density of the EP-hardener–HGMS system to provide greater buoyancy for ESFs. By observing the blue mark in Figure 3, the EP-hardener–HGMS with great viscosity will form some air bubbles in the matrix during the stirring and pouring process. These holes of ESFs are likely to be considered as material defects. Because the holes have no reinforced CFs on the inner wall, they can withstand less pressure than CFR-HEMS. However, these air bubbles could reduce the density of ESFs. In addition, the cost of HGMS and EPS beads is not high and the amount of CF used in the preparation of the ESF is small, which is conducive to its mass production.

Influence of Stacking Volume Fraction of CFR-HEMS on the Compressive Properties of ESFs. Figure 4a shows the influence of the stacking volume fraction of CFR-HEMS on compressive strength of ESFs. The compressive strength without CFR-HEMS of ESF is 33.73 MPa. When the stacking volume fraction of CFR-HEMS is 20%, the compressive strength of ESF is 33.13 MPa. These two samples have higher compressive strengths than the other four samples, but their densities are also relatively large, which also limits their applications in the deep sea. As the stacking volume fraction of CFR-HEMS increases, their compressive strengths are 26.31...
MPa \((40\%)\), 26.27 MPa \((60\%)\), 25.72 MPa \((60\%)\), and 24.95 MPa \((90\%)\). From the set of data, we can draw two conclusions.

(a) As the stacking volume fraction of CFR-HEMS increases, the compressive strength of ESF gradually decreases. When the stacking volume fraction of CFR-HEMS reaches 40\%, the compressive strength of ESF is significantly reduced, and its compressive strength is about 78\% of the ESF without CFR-HEMS. This phenomenon indicates that in the case of achieving low density of ESF, the addition of 40\% CFR-HEMS exceeds the optimal point to keep the ESF’s compressive strength from breaking.

(b) When the stacking volume fraction of CFR-HEMS is larger than 40\%, the compressive strengths of ESFs are 78.0\% \((60\%\) CFR-HEMS), 76.3\% \((80\%\) CFR-HEMS), and 74.0\% \((90\%\) CFR-HEMS) of the ESF without CFR-HEMS. These four data values show that when the stacking volume fraction of CFR-HEMS is larger than 40\%, the compressive strength of ESF gradually decreases but the change tends to be gentle. The stacking volume fraction of CFR-HEMS is no longer the main reason for the change of the compressive strength. As shown in Figure 4c, this phenomenon also prevents the compressive strength of ESF from breaking again.

A smaller density means that ESFs can provide greater buoyancy in the deep sea. Under the condition that the compressive strength of ESFs is not significantly affected, the density of ESFs is smaller relatively, which is beneficial to the application of ESFs. This set of experiments proved that ESFs with 90\% CFR-HEMS have a relatively low density \((0.508 \text{ g/cm}^3)\) and can provide great compressive strength \((24.95 \text{ MPa})\). Therefore, 90\% CFR-HEMS should be the best choice for preparing ESFs.

Influence of Wall Thickness of CFR-HEMS on Compressive Properties of ESFs. The average density of CFR-HEMS increases significantly with the layers increasing, and the density of ESFs greatly. As shown in Figure 5d, when the stacking volume fraction of CFR-HEMS is 90\%, the densities of ESFs are 0.317 g/cm^3 \((0\) layer), 0.403 g/cm^3 \((1\) layer), 0.508 g/cm^3 \((2\) layers), and 0.578 g/cm^3 \((3\) layers). Figure 5c shows that the compressive strengths of the four samples are 7.08 MPa \((0\) layer), 15.16 MPa \((1\) layer), 24.95 MPa \((2\) layers), and 30.56 MPa \((3\) layers). When the volume fractions of CFR-HEMS are 60 and 80\%, the densities and compressive strengths are marked in Figure 5a,b. The following conclusions can be drawn from the set of data.

(a) When CFR-HEMS are not added, the density of ESFs is 0.586 g/cm^3. Thus, the density of the EP-hardener–HGMS system is 0.586 g/cm^3. Figure 5d shows that the density of ESFs prepared by three-layer CFR-HEMS is
very close to that of ESFs without CFR-HEMS. This phenomenon indicates that the addition of three-layer CFR-HEMS cannot significantly reduce the density of ESFs. Compared with the compressive strength of ESFs without CFR-HEMS, ESFs prepared by three-layer CFR-HEMS almost show no improvement. Therefore, three-layer CFR-HEMS are not a good choice for preparing ESFs because of the relatively complex production process.

(b) Under the same stacking volume fraction of CFR-HEMS, the compressive strength of ESFs increases with the layer of CFR-HEMS increasing. It can be seen from Figure 5c that when the CFR-HEMS stacking volume fraction is 90%, the addition of CFR-HEMS with different layers makes the compressive strengths of ESF 1.14 times (1 layer), 2.52 times (2 layers), and 3.38 times (3 layers) times that of the ESF (0 layer). The reason for this phenomenon is that both CFR-HEMS and EP-hardener–HGMS are epoxy-based materials and the two systems are bonded tightly inside the material. The increase of wall thickness makes the structure more stable and CFR-HEMS cannot easily be damaged, so the increase of the layer is conducive to improve the overall compressive strength of ESFs.

(c) As shown in Table 1, when the stacking volume fractions of CFR-HEMS are 60%, 80%, and 90%, the growth rate of the compressive strength shows the same trend as the layers increase. The ratios made from adjacent layers decrease with the layer increasing and the ESFs have the same regulation when the stacking volume fractions of CFR-HEMS are 60 and 80%. The rolling ball method is beneficial to make the CF form the regular structure, which can be seen in the scanning electron microscope (SEM) image. This special structure improves the compressive strength of the one-layer CFR-HEMS compared to the EPS beads significantly, and the improvement is reduced when CFR-HEMS have three layers. With the layers increasing, we could see that the shape of the three-layer CFR-HEMS is not as regular as the one- and two-layer CFR-HEMS. Therefore, it can be seen that when CFR-HEMS have three layers, the growth rate of the compressive strength decreases significantly. When preparing deep-sea buoyancy materials, we need to weigh the density and compressive strength of ESFs according to the requirements of the equipment, so as to choose the appropriate layer of CFR-HEMS for preparation.

### Table 1. Increase Rate of Compressive Strength of ESFs

|        | 1 layer/0 layer | 2 layers/1 layer | 3 layers/2 layers |
|--------|----------------|-----------------|------------------|
| 60%    | 1.913          | 1.303           | 1.300            |
| 80%    | 2.237          | 1.478           | 1.188            |
| 90%    | 2.141          | 1.645           | 1.243            |

**Figure 6.** Influence of the inner diameters of CFR-HEMS on the (a) compressive properties and (b) densities of ESFs (the inner diameters of CFR-HEMS are 7–8, 9–10, and 11–12 mm).

(7–8 mm), 0.508 g/cm³ (9–10 mm), and 0.497 g/cm³ (11–12 mm). From this set of data, the following conclusions can be drawn.

(a) As the inner diameter of CFR-HEMS increases, the average densities of CFR-HEMS will decrease. However, the densities of these kinds of two-layer CFR-HEMS are smaller than those of the EP-hardener–HGMS system (0.586 g/cm³); the addition of these kinds of CFR-HEMS is beneficial to reduce the density of ESFs.

(b) Theoretically, as the particle size increases, the compressive strength of CFR-HEMS decreases, but it can be seen from Figure 6a that the compressive strengths of ESFs are 24.06 MPa (7–8 mm) and 24.95 MPa (9–10 mm); the latter is smaller than the former. The cause of this phenomenon may be that when the particle size is smaller, the amount of CFR-HEMS with the same volume fraction that could be filled into the same area will be more. Much more bubbles are mixed during the
preparation, which may be the reason for weakening the compressive strength of the former ESF.

(c) It can be seen from Figure 6a that the ESF made of CFR-HEMS with inner diameter 11−12 mm has a lower density and could provide larger buoyancy relatively. However, compressive strength and density are two opposing properties in ESFs. As shown in Figure 6a, the ESF made of CFR-HEMS with inner diameter 9−10 mm can work at about 2495 m in the deep sea, while the ESF made of CFR-HEMS with inner diameter 11−12 mm can only work at about 2170 m in the deep sea.

Influence of HGMS Content in the EP-Hardener System on the Compressive Properties of ESFs. As shown in Figure 3, the EP-hardener−HGMS system was first destroyed and the spherical wall of CFR-HEMS remained intact under pressure. The performance of ESFs is also related to the EP-hardener−HGMS system. As shown in Figure 7a, when the stacking volume fraction of CFR-HEMS is 90%, the compressive strengths of ESFs made from different HGMS contents are 19.52 MPa (40%), 20.23 MPa (50%), 24.95 MPa (60%), 15.89 MPa (70%), and 13.74 MPa (75%). From this set of data, it can be seen that the compressive strength of ESFs will first increase and then decrease with the increase of the HGMS content.

When the HGMS content is relatively low, the reasons for the decrease in the compressive strength are as follows. (a) The increase in HGMS content promotes the compressive strength of the EP-hardener−HGMS system to increase. As a result, the compressive strength of the ESF is improved. (b) As shown in Figure 4d, CFR-HEMS will rise in the EP-hardener−HGMS system. As the HGMS content increases, the density of the system is reduced and the viscosity of the system is increased. The rising situation of the CFR-HEMS will be relieved. The distribution of CFR-HEMS in the ESF is more uniform, which improves the compressive strength of the ESF.

However, it does not mean that a higher mass fraction of HGMS is better. When the HGMS contents were 70 and 75%, the compressive strengths of the ESF decreased significantly. The reasons for the phenomenon are as follows. (a) The maximum HGMS content that can be added into the EP-hardener system is 60−70%. During the preparation, when the HGMS content is too large, the HGMS and the EP-hardener system cannot be fully mixed, which leads to the distribution of the HGMS in the EP-hardener being uneven. This kind of ESF is more vulnerable to damage under stress. (b) Excessive HGMS filling greatly reduces the fluidity of the EP-hardener−HGMS system and the difficulty of adding CFR-HEMS is greatly improved. The precured samples exceed the height of the mold, which causes the CFR-HEMS to suffer damage. (c) As shown in Figure 7c, when the HGMS content is too large, some parts of the surface of CFR-HEMS are completely exposed outside of the EP-hardener−HGMS system. The viscosity of the EP-hardener−HGMS system is too large, which leads to the poor binding between the two parts of the ESF.

As shown in Figure 7b, the densities of the five samples are 0.563 g/cm³ (40%), 0.518 g/cm³ (50%), 0.508 g/cm³ (60%), 0.437 g/cm³ (70%), and 0.429 g/cm³ (75%). As the volume fraction of HGMS increases, the density of the ESF decreases. For ESF materials, it cannot completely rely on the increase of the HGMS content to reduce the density of the buoyant materials, and the influence on the compressive strength should be considered. In the experiment, 60% HGMS is the best choice for preparing the high-strength ESF.

Influence of HGMS Types in the EP-Hardener System on the Compressive Properties of ESFs. According to the needs of different products, the HGMS used for preparing the ESF are different. In the experiment, three kinds of HGMS (K1, S32, S38HS) were used. Because the particle size and volume fraction of HGMS used in the experiment are almost the same, the surface contacts between HGMS and the EP-hardener system among the three samples are roughly the same. The difference in the compressive strength of the ESF made in this group is mainly due to the difference in the compressive strength of HGMS themselves. The compressive strength regulation of HGMS is K1 < S32 < S38HS. As shown in Figure 8a, the compressive strengths of ESFs made of K1, S32, and S38HS are...
11.36, 19.72, and 24.95 MPa, which shows the same trend as the compressive strength of HGMS. In the selection of raw materials, the choice of HGMS type has a great influence on the compressive strength of the ESF. When the ESF is used in deeper waters, S38HS should be selected as the raw material so that it can withstand a larger water pressure relatively.

From Figure 8b, it can be seen that the densities of the ESF made by K1, S32, and S38HS were 0.434, 0.454, and 0.508 g/cm³, respectively. The ESF made of S38HS has a higher compressive strength (24.95 MPa) but a higher density (0.508 g/cm³) relatively. For deep-sea equipment, low density is a necessary factor. The decrease in density also means a reduction in the compressive strength.

Influence of HGMS Types in the EP-hardener system on the Compressive Properties of ESF. As shown in Figure 8b, the densities of ESFs made from CFR-HEMS prepared by 30 AW, 100 AW, and 300 AW CF are 0.427, 0.462, and 0.508 g/cm³, respectively. The density of the CF is about 1.76 g/cm³, and the wire diameter is about 7 μm. CFs with different meshes have different aspect ratios, which are about 70:1 (30 AW), 14:1 (100 AW), and 6:1 (300 AW). From Figure 9c, it can be seen that as the mesh size increases, the wall of CFR-HEMS becomes denser. The dense and smooth coating improved the compressive strength of both CFR-HEMS and the ESF. The ESF prepared by 300 AW CF has the highest compressive strength (24.95 MPa) among the three samples (Figure 10).

Influence of CF Types of CFR-HEMS on the Compressive Properties of ESF. As shown in Figure 9b, the densities of ESFs made from CFR-HEMS prepared by 30 AW, 100 AW, and 300 AW CF are 0.427, 0.462, and 0.508 g/cm³, respectively. The density of the CF is about 1.76 g/cm³, and the wire diameter is about 7 μm. CFs with different meshes have different aspect ratios, which are about 70:1 (30 AW), 14:1 (100 AW), and 6:1 (300 AW). From Figure 9c, it can be seen that as the mesh size increases, the wall of CFR-HEMS becomes denser. The dense and smooth coating improved the compressive strength of both CFR-HEMS and the ESF. The ESF prepared by 300 AW CF has the highest compressive strength (24.95 MPa) among the three samples (Figure 10).

Influence of CF Content in EP-Hardener–HGMS on the Compressive Properties of ESF. In the experiment, 1, 3, 5, 7, and 9% CFs were added to the EP-hardener–HGMS system to prepare the CF-reinforced EP-hardener–HGMS system (CF-R-epoxy). There is no significant change in the density of the ESF, which is similar to the density of the ESF without CF added to the matrix. Therefore, it can be seen that the addition of CF with a lower mass fraction in the matrix has a little effect on the density of the ESF. The compressive strength of the ESF without CF in the EP-hardener–HGMS system is 24.95 MPa. When the CF contents in the matrix are 1, 3, 5, 7, and 9%, the compressive strengths of the ESF are 26.21, 26.63, 25.43, 26.73, and 25.72 MPa, respectively. It can be seen from the SEM image that the CF distribution is relatively thin, and the content of CF added into the matrix is not large enough to make the CF form the...
special structure. However, the addition of CF improves the performance of the EP-hardener system. From this set of data, it can be seen that when CF is added to the EP-hardener–HGMS system, the compressive strength could be improved. The compressive strength of the ESF fluctuates with the increase of the CF content. Among the five samples, when the mass fraction of the CF is 7%, the compressive strength improvement of the ESF is obvious relatively and the compressive strength is 7.13% higher than that of the ESF without CF in the EP-hardener–HGMS system.

**SEM Image of the Multiphase ESF.** By observing the compressed ESF in Figure 3, the EP-hardener–HGMS system and CFR-HEMS are still found to be closely combined at the destruction site and the main cause of ESF fragmentation is the fracture of the matrix. As shown in Figure 11a, the wall thickness of CFR-HEMS is about 505 μm, and there is no gap between the EP-hardener–HGMS system and CFR-HEMS. The spherical wall composed of the CF and the EP-hardener system is very uniform, which makes CFR-HEMS more conducive to force transmission and increases the overall compressive strength of the ESF.

The CFs in the spherical wall of the CFR-HEMS formed by the rolling ball method are uniform and dense. The orientation of CFs is mostly on the tangent plane with the spherical wall, and there are almost no CFs in the direction of the CFR-HEMS diameter, which is more conducive to the force transmission of CFR-HEMS and the ESF. Figure 11b shows the dispersion diagram of carbon fiber in the spherical wall of CFR-HEMS. The forces (centrifugal force and pressure) can also make the carbon fibers form a CF network throughout the macrosphere epoxy matrix, and the fibers are held together by force. When the macrospheres were used in the ESF, the structure of the CF network can make the macrospheres have great compressive strength. When ESFs are used in deepwater oil exploration, they are under enormous water pressure from all directions. The pressure can transfer through the carbon fiber network of the macrosphere, so most of the forces can be offset. Only a very small force transfers along the axial direction (z-direction), so tremendous pressure is needed to destroy the macrosphere. Figure 11c shows the SEM image of the CF in the EP-hardener–HGMS system. It can be seen from Figure 11c that the CF is
connected to the matrix tightly, which promoted the improvement of the compressive strength of the ESF to some extent.

**CONCLUSIONS**

(a) From the present study, we can see that as the stacking volume fraction of CFR-HEMS increases, the compressive strength of the ESF gradually decreases. The ESF with 90% CFR-HEMS has a low density (0.508 g/cm³) relatively and can provide great compressive strength (24.95 MPa). For achieving the lowest density of ESF, 90% CFR-HEMS should be the best choice for preparing the ESF.

(b) The compressive strength of the ESF increases with the layer of CFR-HEMS increasing under the same stacking volume fraction. However, when CFR-HEMS have three layers, the densities of the ESF cannot be reduced significantly and the compressive strengths almost have no improvement. This phenomenon indicates that the addition of three-layer CFR-HEMS is not a good choice for preparing the ESF.

(c) When CFR-HEMS have two layers, the ESF prepared by CFR-HEMS with inner diameter 9−10 mm has the highest compressive strength (24.95 MPa) and the ESF prepared by CFR-HEMS with inner diameter 11−12 mm has the lowest density (0.497 g/cm³). Therefore, we need to choose the better CFR-HEMS for preparing the ESF according to the ESF required by different deep-sea equipment.

(d) The compressive strengths of the ESF made from different HGMS contents are 19.52 MPa (40%), 20.23 MPa (50%), 24.95 MPa (60%), 15.89 MPa (70%), and 13.74 MPa (75%). The compressive strength of the ESF will first increase and then decrease with the increase of the HGMS content. In the experiment, 60% HGMS is the best choice for preparing the high-strength ESF.

(e) The densities of ESFs made by K1, S32, and S38HS are 0.434, 0.454, and 0.508 g/cm³. The ESFs prepared by S38HS has the highest compressive strength (24.95 MPa) among the three kinds of ESFs.

(f) The densities of ESFs made from CFR-HEMS prepared by 30 AW, 100 AW, and 300 AW CF are 0.427, 0.462, and 0.508 g/cm³, respectively. Although using 300 AW CF to prepare CFR-HEMS makes the density of ESF higher than the other two samples, this kind of ESF has the highest compressive strength (24.95 MPa).

(g) In this experiment, 1, 3, 5, 7, and 9% CFs were added to the EP-hardener−HGMS system. When the mass fraction of the CF is 7%, the compressive strength improvement of the ESF is the highest and the compressive strength (26.73 MPa) is 7.13% higher than that of the ESF without CF in the EP-hardener−HGMS system. We can see from these five samples that adding CF into the EP-hardener−HGMS system could keep the density almost unchanged and improve the compressive strength to some extent.

**EXPERIMENTAL SECTION**

**Materials.** The resin used for the experiment was an EPOLAM 2070 resin. EPOLAM 2070 is an amber epoxy resin. The Brookfield viscosity and density of the resin are 2800 mPa·s and 1.17 g/cm³ at 25 °C, respectively. The color of the curing agent is dark amber. Both of the resin and the curing agent are manufactured by AXSON Technologies Shanghai Co. Ltd, China.

K1, S32, and S38HS used for preparing the EP-hardener−HGMS are three kinds of white HGMS. The densities of the three kinds of HGMS are 0.15 g/cm³ (K1), 0.32 g/cm³ (S32), and 0.38 g/cm³ (S38HS). Their compressive strengths are 1.72, 13.78, and 37.90 MPa, respectively. The three kinds of HGMS are all manufactured by Minnesota Mining and manufacturing (3 M company).

The EPS beads selected for the study are produced by Hangzhou Hangchao Packaging Materials Co. Ltd, China. The density of the EPS beads is about 10 kg/m³.

The CF used for preparing the CFR-HEMS and adding into the EP-hardener−HGMS system is manufactured by Nanjing Weida Composite Materials Co. Ltd., China. The density of the CF is about 1.76 g/cm³, and the wire diameter is about 7 μm.

**Preparation of CF-Reinforced Hollow Epoxy Macro-sphere Systems (CFR-HEMS).** CFR-HEMS was prepared by the rolling ball method. The preparation process is as follows.

Three parts of epoxy resin and one part of curing agent were measured into a defoaming mixer and stirred fully to form the EP-hardener system. A certain amount of EPS beads was weighed out and poured into the defoaming mixer, and the mixture was fully stirred at the same speed. After the EPS bead surfaces were evenly covered by the EP-hardener system, the coated EPS beads were poured into a rotating ball machine. The CF powder was sprinkled over the coated EPS beads in the machine. When the surface of the beads was completely covered with CF powder, the excess powder on the surface was separated. The coated EPS beads were poured into a tray and then put into a 50 °C oven. The preparation process of one-layer CFR-HEMS was considered completed after the epoxy resin was cured completely. According to the same step, one-layer CFR-HEMS were poured into the EP-hardener system and the CF powder was sprinkled over the coated CFR-HEMS to prepare two- and three-layer CFR-HEMS (Figure 12).

**Figure 12. Preparation process of CFR-HEMS.**

**Preparation of Multiphase ESFs.** Multiphase ESFs were prepared by the pouring method and the compression modeling method. The preparation process is as follows.

Three parts of epoxy resin and one part of curing agent were measured and stirred well. HGMS with the volume fraction of 60% were added to the EP-hardener system and then CFR-HEMS were mixed into the EP-hardener−HGMS system. If the stirring speed is too fast, the EP-hardener−HGMS system will become more porous. After the CFR-HEMS were evenly distributed in the EP-hardener−HGMS system, the mixture was poured into a mold coated with a release agent. The CFR-HEMS should be poured into the mold completely, and the composite was placed into a hot press to cure at 100 °C for 1 h and then in a cold press for 15 min. The preparation of the multiphase ESF was considered completed after the epoxy resin was cured completely (Figure 13).

**Preparation of ESFs Filled with CFR-HEMS with Different Stacking Volume Fractions.** To study the effect of stacking volume fractions of CFR-HEMS on the mechanical
properties and density of ESFs, CFR-HEMS of different volume fractions were weighed and added to the EP-hardener−HGMS system. The stacking volume fraction of CFR-HEMS filled into the mold completely is 100%. Although there are holes in the group of CFR-HEMS, it is difficult to mix 100% CFR-HEMS with the EP-hardener−HGMS system into the mold. For the feasibility of the experiment, 0, 20, 40, 60, 80, and 90% CFR-HEMS were measured and added into the EP-hardener−HGMS system. Table 2 shows six samples of ESF filled with CFR-HEMS with different stacking volume fractions.

Preparation of ESFs Filled with CFR-HEMS of Different Wall Thicknesses. CFR-HEMS with different layers will affect the compressive strength and density of CFR-HEMS. To study the effect of CFR-HEMS with different wall thicknesses on the properties of ESFs, 90% CFR-HEMS with 0−3 layers were measured and were mixed with the EP-hardener−HGMS system. Table 3 shows four samples of ESF filled with CFR-HEMS with different wall thicknesses.

Preparation of ESFs Filled with CFR-HEMS with Different Inner Diameters. To study the effect of CFR-HEMS with different inner diameters on ESFs, CFR-HEMS with inner diameters of 7−8, 9−10, and 11−12 mm were added to the EP-hardener−HGMS system. Table 4 shows four samples of ESF filled with CFR-HEMS with different inner diameters (Table 4).

Preparation of ESFs with Different HGMS Volume Fractions and Types. Volume fractions and types of HGMS determine the viscosity of the EP-hardener−HGMS system and affect the curing of the EP-hardener−HGMS system. To study the density and compressive strength of ESFs with different contents of HGMS, five sample volume fractions of HGMS of 40, 50, 60, 70, and 75% were prepared. In addition, three kinds of

---

Table 2. Six Samples of ESFs Filled with CFR-HEMS of Different Stacking Volume Fractions

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP |
|-----------------------------------------|-------------------------------------|----------------------------------|------------------|-----------------------|-----------------------|------------------------|
| 1                                       | 0                                   | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |
| 2                                       | 20                                  | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |
| 3                                       | 40                                  | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |
| 4                                       | 60                                  | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |
| 5                                       | 80                                  | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |
| 6                                       | 90                                  | 9–10                            | 60               | S38HS                 | 300 AW                 | 0                      |

Table 3. Four Samples of ESFs Filled with Different Wall Thickness CFR-HEMS

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP |
|-----------------------------------------|-------------------------------------|----------------------------------|------------------|-----------------------|-----------------------|------------------------|
| 1                                       | 60%/80%/90%                         | 0                                | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |
| 2                                       | 60%/80%/90%                         | 1                                | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |
| 3                                       | 60%/80%/90%                         | 2                                | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |
| 4                                       | 60%/80%/90%                         | 3                                | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |

Table 4. Three Samples of ESFs Filled with CFR-HEMS with Different Inner Diameters

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP |
|-----------------------------------------|-------------------------------------|----------------------------------|------------------|-----------------------|-----------------------|------------------------|
| 1                                       | 60                                  | 2                               | 7–8              | 60                    | S38HS                 | 300 AW                 | 0                      |
| 2                                       | 60                                  | 2                               | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |
| 3                                       | 60                                  | 2                               | 11–12            | 60                    | S38HS                 | 300 AW                 | 0                      |

Table 5. Five Samples of ESFs Filled with the HGMS-EP System with Different HGMS Contents

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP |
|-----------------------------------------|-------------------------------------|----------------------------------|------------------|-----------------------|-----------------------|------------------------|
| 1                                       | 90                                  | 2                               | 9–10             | 40                    | S38HS                 | 300 AW                 | 0                      |
| 2                                       | 90                                  | 2                               | 9–10             | 50                    | S38HS                 | 300 AW                 | 0                      |
| 3                                       | 90                                  | 2                               | 9–10             | 60                    | S38HS                 | 300 AW                 | 0                      |
| 4                                       | 90                                  | 2                               | 9–10             | 70                    | S38HS                 | 300 AW                 | 0                      |
| 5                                       | 90                                  | 2                               | 9–10             | 75                    | S38HS                 | 300 AW                 | 0                      |
The compressive properties of ESFs were tested by an electronic universal testing machine (CMT5350, Shenzhen Suns Technology Co. Ltd., China). This experiment used GB/T16491–2008 as the standard. Scanning electron microscopy (SEM) (JEM-4701, JEOL, Japan) was used to observe the spherical wall of CFR-HEMS, the binding of CFR-HEMS with EP-hardener–HGMS, and the distribution of CF in the EP-hardener–HGMS system. The sample to be measured must be relatively thin and sprayed with gold to make it highly conductive and easy to observe.

### AUTHOR INFORMATION

**Corresponding Authors**

**Jinhong Yu** — Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China; [orcid.org/0000-0001-9134-7568]; Email: yujinhong@nimte.ac.cn

**Yuantao Zhao** — Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China; Email: zhaoyt@shmtu.edu.cn

**Wenge Li** — Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China; Email: wgli@shmtu.edu.cn

**Authors**

**Xinfeng Wu** — College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China

**Yuan Gao** — College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China; [orcid.org/0000-0001-6684-364X]

**Ying Wang** — Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China

**Tao Jiang** — Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China; [orcid.org/0000-0002-6631-2192]

**Ke Yang** — School of Materials Science and Engineering, Central South University, Changsha 410083, China

Complete contact information is available at:

Table 6. Three Samples of ESFs Filled with the HGMS-EP System with Different HGMS Types

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP (%) |
|----------------------------------------|-------------------------------------|-------------------------------|-----------------|------------------------|------------------------|--------------------------|
| 1                                      | 60                                  | 2                             | 9–10            | 60                     | K1                     | 30 AW                    |
| 2                                      | 60                                  | 2                             | 9–10            | 60                     | S32                    | 300 AW                   |
| 3                                      | 60                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |

Table 7. Three Samples of ESFs Filled with HEMS Reinforced by CFs of Different Meshes

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP (%) |
|----------------------------------------|-------------------------------------|-------------------------------|-----------------|------------------------|------------------------|--------------------------|
| 1                                      | 60                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
| 2                                      | 60                                  | 2                             | 9–10            | 60                     | S38HS                  | 100 AW                   |
| 3                                      | 60                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |

Table 8. Five Samples of ESFs Reinforced by Adding CFs of Different Qualities into the HGMS-EP System

| stacking volume fractions of CFR-HEMS (%) | wall thicknesses of CFR-HEMS (layers) | inner diameters of CFR-HEMS (mm) | HGMS contents (%) | HGMS types of CFR-HEMS | HGMS types of CFR-HEMS | CF contents in HGMS-EP (%) |
|----------------------------------------|-------------------------------------|-------------------------------|-----------------|------------------------|------------------------|--------------------------|
| 1                                      | 90                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
| 2                                      | 90                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
| 3                                      | 90                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
| 4                                      | 90                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
| 5                                      | 90                                  | 2                             | 9–10            | 60                     | S38HS                  | 300 AW                   |
Author Contributions
X.W. and Y.G. contributed equally to this work.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the Project Funded by China Postdoctoral Science Foundation (2017M611757), the Special Fund of the National Natural Science Foundation of China (51573201), the Shanghai Science and Technology Talent Planning Project (19QB1402200), and the Capacity Improvement Project for Municipal Universities in Shanghai by Shanghai Science and Technology Commission (19040501800).

REFERENCES
(1) Gupta, N.; Ye, R.; Porfiri, M. Comparison of tensile and compressive characteristics of vinyl ester/glass microballoon syntactic foams. Composites, Part B 2010, 41, 236–245.
(2) Zhang, Y.; Ding, Z. J.; Wang, Y. F.; Zhao, Q. X.; Qin, S. J. Determining the Damage Mechanisms for Buoyancy Materials of Deep-Sea Manned Submersibles. J. Coastal Res. 2019, 35, 996–1002.
(3) Le Gall, M.; Choqueuse, D.; Le Gac, P. Y.; Davies, P.; Perreux, D. Novel mechanical characterization method for deep sea buoyancy material under hydrostatic pressure. Polym. Test. 2014, 39, 36–44.
(4) Chen, Z. P.; Xu, C.; Ma, C. Q.; Ren, W. C.; Cheng, H. M. Lightweight and Flexible Graphene Foam Composites for High-Performance Electromagnetic Interference Shielding. Adv. Mater. 2013, 25, 1296–1300.
(5) Ren, S.; Hu, X. X.; Ren, H. T.; Wang, M. C.; Guo, A. R.; Liu, J. C.; Du, H. Y.; Xian, L. Development of a buoyancy material of hollow glass microspheres/SiO2 for high-temperature application. J. Alloys Compd. 2017, 721, 213–219.
(6) Priede, I. G. Buoyancy of gas-filled bladders at great depth. Deep Sea Res., Part I 2018, 132, 1–5.
(7) Fatallah, E.; Qi, H.; Tong, L. L.; Helal, M. Design optimization of lay-up and composite material system to achieve minimum buoyancy factor for composite elliptical submersible pressure hull. Compos. Struct. 2015, 121, 16–26.
(8) Li, J. B.; Yang, X.; Xiu, H. J.; Dong, H. L.; Song, T.; Ma, F. Y.; Feng, P.; Zhang, X. F.; Kozlak, E.; Ji, Y. Structure and performance control of plant fiber based foam material by fibrillation via refining treatment. Ind. Crops Prod. 2019, 128, 186–193.
(9) Aflahb, L. O.; Mutalib, N. A. A.; Ariff, Z. M. Fabrication and characterization of two-phase syntactic foam using vacuum assisted mould filling technique. J. Mater. Res. Technol. 2019, 8, 3843–3851.
(10) Zafar, M. T.; Zarrinbaksh, N.; Mohanty, A. K.; Misra, M.; Maiti, S. N.; Ghosh, A. K. Biocomposites based on poly(lactic acid)/willow-fiber and their injection moulded microcellular foams. Express Polym. Lett. 2016, 10, 176–186.
(11) Yano, Y.; Takagawa, S. Exploratory study on engineering ceramics pressure hulls for deep-sea submergence services. Mar. Technol. Soc. J. 2005, 39, 49–55.
(12) Yu, Q. Y.; Zhao, Y.; Dong, A. Q.; Li, Y. Mechanical properties of EPS filled syntactic foams prepared by VARTM. Composites, Part B 2018, 136, 126–134.
(13) Shams, A.; Panteghini, A.; Bardella, L.; Porfiri, M. A micromechanical model to study failure of polymer-glass syntactic foams at high strain rates. Comput. Mater. Sci. 2017, 135, 189–204.
(14) Yang, G.; Liu, X. Y.; Lipik, V. Evaluation of silica aerogel-reinforced polyurethane foams for footwear applications. J. Mater. Sci. 2018, 53, 9463–9472.
(15) Li, J. H.; Wei, L. Q.; Leng, W. Q.; Hunt, J. F.; Cai, Z. Y. Fabrication and characterization of cellulose nanofibrils/epoxy nano-composite foam. J. Mater. Sci. 2018, 53, 4949–4960.
(16) Gavin, C.; Verbeek, C. J. R.; Lay, M. C. Morphology and compressive behaviour of foams produced from thermoplastic protein. J. Mater. Sci. 2018, 53, 15703–15716.
(17) Carranza, I.; Crocombe, A. D.; Mohagheghian, I.; Smith, P. A.; Sordon, A.; Meeks, G.; Santoni, C. Characterising and modelling the mechanical behaviour of polymeric foams under complex loading. J. Mater. Sci. 2019, 54, 11328–11344.
(18) Bo, C. Y.; Hu, L. H.; Chen, Y.; Yang, X. H.; Zhang, M.; Zhou, Y. H. Synthesis of a novel cardanol-based compound and environmentally sustainable production of phenolic foam. J. Mater. Sci. 2018, 53, 10784–10797.
(19) Danesh, A.; Mosaberpanah, M. A. Formation mechanism and applications of cenospheres: a review. J. Mater. Sci. 2020, 55, 4539–4557.
(20) Kartal, M. E.; Dugdale, L. H.; Harrigan, J. J.; Siddiq, M. A.; Pokrajac, D.; Mulvihill, D. M. Three-dimensional in situ observations of compressive damage mechanisms in syntactic foam using X-ray microcomputed tomography. J. Mater. Sci. 2017, 52, 10186–10197.
(21) Brown, J. A.; Carroll, J. D.; Huddleston, B.; Casias, Z.; Long, K. N. A multiscale study of damage in elastomeric syntactic foams. J. Mater. Sci. 2018, 53, 10479–10498.
(22) Meng, Y.; Li, H.; Zeng, J.; Li, X. G.; Gao, X. A novel potential application of SiC ceramic foam material to distillation: Structured corrugation foam packing. Chem. Eng. Res. Des. 2019, 150, 254–262.
(23) Gao, X.; Li, X. G.; Liu, X.; Li, H.; Yang, Z. M.; Zhang, J. S. A novel potential application of SiC ceramic foam material to distillation: foam monolithic tray. Chem. Eng. Sci. 2015, 135, 489–500.
(24) Panteghini, A.; Bardella, L. On the compressive strength of glass microballoons-based syntactic foams. Mech. Mater. 2015, 82, 63–77.
(25) Bardella, L.; Malanca, F.; Ponzo, P.; Panteghini, A.; Porfiri, M. A micromechanical model for quasi-brittle compressive failure of glass-microballoons/thermoset-matrix syntactic foams. J. Eur. Ceram. Soc. 2014, 34, 2605–2616.
(26) Nij, J.; Li, G. Q.; A CaO enhanced rubberized syntactic foam. Composites, Part A 2008, 39, 1404–1411.
(27) Liang, J. Z. Estimation of thermal conductivity for polypropylene/hollow glass bead composites. Composites, Part B 2014, 56, 431–434.
(28) Wang, A. X.; Chu, D. Q.; Wang, L. M.; Mao, B. G.; Sun, H. M.; Ma, Z. C. Template-free hydrothermal synthesis of copper hollow microspheres: microstructure, formation mechanism and compression plasticity. RSC Adv. 2014, 4, 7545–7548.
(29) Kim, M. W.; Kwon, S. H.; Park, H.; Kim, B. K. Glass fiber and silica reinforced rigid polyurethane foams. Express Polym. Lett. 2017, 11, 374–382.
(30) Lin, T. C.; Gupta, N.; Talalayev, A. Thermoanalytical characterization of epoxy matrix-glass microballoon syntactic foams. J. Mater. Sci. 2009, 44, 1520–1527.
(31) Yu, M.; Zhu, P.; Ma, Y. Q. Effects of particle clustering on the tensile properties and failure mechanisms of hollow spheres filled syntactic foams: A numerical investigation by microstructure based modeling. Mater. Des. 2013, 47, 80–89.
(32) An, X. Z.; He, S. S.; Feng, H. D.; Qian, Y. Packing densification of binary mixtures of spheres and cubes subjected to 3D mechanical vibrations. Appl. Phys. A 2015, 118, 151–162.
(33) Kristiansen, K. D.; Wouterse, A.; Philipse, A. Simulation of random packing of binary sphere mixtures by mechanical contraction. Physica A 2005, 358, 249–262.
(34) Gupta, N.; Woldsenbet, E.; Kishore. Compressive fracture features of syntactic foams-microscopic examination. J. Mater. Sci. 2002, 37, 3199–3209.
(35) Wu, X. F.; Tang, B.; Yu, J. H.; Cao, X.; Zhang, C. Y.; Lv, Y. G. Preparation and Investigation of Epoxy Syntactic Foam (Epoxy/ Graphite Reinforced Hollow Epoxy Macropolymer/Hollow Glass Microsphere Composite). Fibers Polym. 2018, 19, 170–187.

https://pubs.acs.org/10.1021/acsomega.0c01744
(36) Wu, X. F.; Wang, Y.; Yang, X. R.; Yu, J. H.; Wang, L. C.; Hou, S. J.; Jiang, P. K. A “rolling ball method” to make glass fiber reinforced hollow epoxy macrospheres used for a three phase epoxy syntactic foam. RSC Adv. 2015, 5, 61204−61217.

(37) Ciardiello, R.; Drzal, L. T.; Belingardi, G. Effects of carbon black and graphene nano-platelet fillers on the mechanical properties of syntactic foam. Compos. Struct. 2017, 178, 9−19.

(38) Wu, X. F.; Dong, L. H.; Zhang, F. H.; Zhou, Y.; Wang, L. P.; Wang, D. S.; Yin, Y. S. Preparation and Characterization of Three Phase Epoxy Syntactic Foam Filled With Carbon Fiber Reinforced Hollow Epoxy Macrospheres and Hollow Glass Microspheres. Polym. Compos. 2016, 37, 497−502.

(39) Samsudin, S. S.; Ariff, Z. M.; Zakaria, Z.; Bakar, A. A. Development and characterization of epoxy syntactic foam filled with epoxy hollow spheres. Express Polym. Lett. 2011, 5, 653−660.

(40) Noguchi, T.; Asano, K.; Hiratsuka, S.; Miyahara, H. Trends of composite casting technology and joining technology for castings in Japan. Int. J. Cast. Met. Res. 2008, 21, 219−225.

(41) Wu, H.; Zhao, G.; Wang, J.; Wang, G.; Zhang, W. Effects of process parameters on core-back foam injection molding process. Express Polym. Lett. 2019, 13, 390−405.