Preparation and Properties of Anti-Insulation Integrated Phenolic Resin Composites

Duan Ge1, Minxian Shi1, Yalin Yao2, Shican Jiang1, Dongpei He1 and Zhixiong Huang1

1School of Materials Science and Engineering, Wuhan University of Technology, NO. 122 Luoshi Road, Wuhan 430070, China.
2Beijing FRP Research and Design Institute Co. Ltd, No. 1 Xinglong South Street, Yanqing District, Beijing 102101, China.
Email: minxianshi@whut.edu.cn

Abstract. This paper mainly studies a kind of anti-insulation integrated light phenolic resin composite material among many thermal protective materials. The study found that the addition of ceramic microspheres can significantly reduce the density of the sheet, improve the thermal insulation properties of the material, and also improve the other properties of the material. Studies have shown that the residual rate increases with increasing volume fraction, and the ablation performance is optimal at a percentage of 30%.

1. Introduction
In recent years, research on the addition of hollow microspheres into the system in the field of integrated anti-insulation has attracted much attention. Qin Yan et al [1] used phenolic resin as the matrix, and prepared low-density anti-insulation composite materials with good thermal insulation properties and excellent ablation performance under high temperature conditions by adding functional filler microbeads and porcelain auxiliaries. The porous fiber porous matrix is used as the matrix, and the phenolic resin is filled in the inner hole of the porous fiber skeleton, which fully utilizes the advantages of the skeleton and the resin. Bahramian et al. [2] prepared a porous fiber-based phenolic resin ablative composite material. Chen Yongxin [3] and other phenolic foams with hollow glass microspheres were prepared by compression molding. When the mass fraction of hollow glass microspheres was 10% of the resin mass, compared with pure phenolic foam, it was not pretreated and pretreated. The hollow glass microsphere-reinforced phenolic foam increased the residual carbon rate at 880 °C by 5.4% and 6.4%, respectively. The untreated and pretreated hollow glass microspheres enhanced the phenolic foam compressive strength by 282.9% and 328.6%, respectively, compared with the pure phenolic foam. The surface insulation of the fuel tank and solid rocket of the US Space Shuttle [4] uses a sprayable composite foam coating of hollow glass beads as an excellent thermal insulation material.

Adding hollow microspheres can ensure the strength requirements of materials to a certain extent while reducing weight and preventing heat insulation. Gao and his team members [5] filled glass microspheres into silicone rubber foam, effectively reducing the average pore size and increasing the hardness and tensile strength of the material. Wouterson et al. created different microstructures by using three different types of microspheres and by volume fraction of 0 to 50% of the microspheres. The results show that the bending strength decreases with increasing filler content, and the bending strength behavior is not affected. The effect of the component microspheres. Huang et al [6] found that the flexural strength and fracture toughness of microsphere-filled phenolic composite foam modified
by glutaraldehyde and siloxane decreased less than that of materials without added microspheres.

2. Experimental
Firstly, the boron phenolic resin solid is pulverized into a powder and then dissolved in absolute ethanol. The mass ratio of the boron phenolic resin to the absolute ethanol is 1:1, and then placed in an oven at 76 °C, and stirred once every 20 minutes until the solid boron phenolic resin is completely dissolved in ethanol. Next, the ceramic microspheres were surface treated with a silane coupling agent KH-550.

According to the number of layers and the area of each layer, the quality of the fiber cloth is weighed. The mass of the boron phenolic resin after dissolution was 3.5 times that of the fiber cloth. The percentage of ceramic microspheres added was determined to be 0%, 10%, 20%, 30%, 40% depending on the quality of the resin. The uniformly mixed resin was coated on the fiber cloth. Allow the air to stand until the prepreg is not sticky, cut, overlap.

Two thickness plates (4mm and 10mm thick) were produced by compression molding. The number of layers of prepreg was 20 and 40, respectively. The content of ceramic microspheres was 0%, 10%, 20%, 30%, 40%. Plate. The 20-layer and 40-layer prepreg are respectively laminated together. The prepreg of the 4 mm plate has a size of 9 mm*14 mm, and the prepreg of the 10 mm thick plate has a size of 9 mm*9 mm.

3. Results and Discussion

3.1. Density
The density test was carried out according to GB/T 1463-2005. Since the ceramic microspheres are added, and the inside of the microspheres is hollow, its density is lower than that of the resin, so that a lightweight effect can be obtained, and a composite sheet having a low density relative to the original sheet material can be obtained. Density is measured by weighing, calculating the volume, and determining the density. The density of composite sheets with volume fractions of 0, 10%, 20%, 30%, and 40% ceramic microspheres is shown in Figure 1.

![Figure 1. Panel density of each compound](image)

It can be seen from the above that the ceramic microsphere content of 10%, 20%, 30% of the sheet density is less than 0%. When the ceramic microsphere content reaches 40%, the composite sheet density is higher than 0%. Studies have shown that the addition of ceramic microspheres can
Effectively achieves a light weight effect, a reduced specific gravity, and an optimum content of about 20%.

3.2. Mechanical Properties Test (Bending Strength Test)
In this experiment, 0, 10%, 20%, 30%, and 40% of the sheets were subjected to heat treatment at three temperatures (600 °C, 800 °C, and 1000 °C) except for normal temperature, and a three-point bending test was performed. For the bending test, the universal material testing machine RGM-4100 was used in accordance with the GB/T 1449-2005 standard. The flexural modulus is calculated according to the equation. The average value is required for each set.

\[ E = \frac{FS^3}{4\Delta WB^3} \]  \hspace{1cm} (1)
(Where \( F \) is the maximum force, \( S \) is the support span, \( W \) is the width, \( B \) is the thickness of the specimen, and \( \Delta \) is the instantaneous displacement according to the instantaneous load.)

![Bending strength after ablation of each formulation sheet](image)

Figure 2. Bending strength after ablation of each formulation sheet

It can be intuitively seen from the Figure 3.2 that as the heat treatment temperature increases, the bending strength of the sample decreases remarkably. And as the volume fraction of ceramic microspheres increases, the curve basically shows a downward trend, and all the samples fail at the center of the support span.

3.3. Section Topography Scanning
After the bending test is completed, the section is scanned by SEM, and the JSM-IT300 scanning electron microscope is used to measure the observation section, which is helpful for analyzing the reason of the strength. The sample is in the form of a block and is less than 2 cm * 2 cm in size. Observing the cross section by scanning electron micrograph, we can see the brittle fracture of the resin after curing and the breakage of the fiber. Some spherical voids can also be seen in Figure 3, which is caused by the debonding of the microspheres during the bending process. The interaction between the microsphere and the resin is lower than the strength at which the microsphere itself is destroyed. The sample has several components: hollow ceramic microspheres, a phenolic resin matrix, an interface between the microspheres and the matrix, an interface between the resin system and the fibers, and internal voids, and the internal voids are introduced by the molding process, which is unavoidable. When subjected to a load, local phenomena include cracks at the beginning and through the internal void, cracking of the interface, cracking of the microspheres and the resin itself. The crack
begins with the internal void formed during the solidification process. When the crack begins, it will propagate to the stage where the lowest energy is needed, the phase that provides the least obstacle to the propagation of the crack front. Due to the introduction of ceramic microspheres, more interfaces were introduced. Although the coupling agent improved the interface, the existence of the interface gave the path of crack propagation. As shown in Figure 3, the cracks along the resin and microspheres can be seen. Interface extension. Therefore, the crack is more likely to propagate along the interface, which also leads to the debonding of the resin, the ceramic microspheres, and the fiber, so that the layering is easy, and the effect of the resin transfer load is greatly reduced, which is also easy to cause stress concentration at the defect. It is also shown in Figure 4 that when the microsphere volume fraction is small, the resin system and fiber interface are much better than the microspheres. On the other hand, the more ceramic microspheres, the more hollow portions are introduced, and the bending strength of the gas inside the ceramic microspheres is necessarily lower than the bending strength of the composite material. Therefore, these aspects lead to the fact that the more the filler content at the four temperatures, the lower the bending strength is substantially. At 40% of the formulation, the flexural strength of the composite sheet slightly rebounds. This may be because 40% of the volume fraction is larger, the content of the microspheres is much, and it is easy to agglomerate, as shown in Figure 4(d), the ceramic microspheres. The agglomeration and fragmentation of many microspheres can be seen on the section of the plate with 40% of the integral number. The microspheres are compressed and destroyed, that is, crushed during the molding process, so that part of the hollow gas in the molding is discharged outside the plate, reducing the inner hollow portion has a slight increase in strength, but cracks and voids are introduced, the interface is deteriorated, and the strength is lower than the original state.

Figure 3. Example of section crack extension

Figure 4. Sectional morphology of four formula sheets after bending failure

At the same time, it can be clearly seen that as the heat treatment temperature increases, the bending strength of the plates of each group has been greatly reduced. This may be because the ablation at high temperature causes the resin to decompose and the fibers are damaged. Cracks and voids appear to increase. Figure 4 also shows that the resin of various formulations is severely pulverized at 600 °C, the surface of the fiber becomes rough, and the microspheres are not greatly affected. In the composite material, the main bearing role is the fiber, and the effect of the resin transmitting stress after the heat treatment is not exerted, so the bending strength is greatly lost. However, compared with 0%, that is, the material without filler, the bending strength of the ceramic microspheres 20%, 30%, 40% is less, and the bending strength loss of the 30% sample is the smallest.
Observe the cross-sectional morphology of the heat treated at 600 °C in 30% and 10% of Figure 5(a) (e). It can be seen that the decomposition of the resin is better than 10% in the case of an increase in the content of the microspheres (30%). This may be attributed to the addition of ceramic microspheres, the introduction of a hollow structure, the heat is not easy to transport, the thermal insulation properties of the material are improved, and the heat loss of the internal fiber and resin system is reduced. Observe the heat-treated sample, as shown in Figure 5, to maintain the original shape. Studies have shown that the addition of ceramic microspheres can improve the heat resistance of the sample to a certain extent, and has a certain ability to withstand bending.

![Figure 5. Curved failure section before and after heat treatment of four formula plates](image)

3.4. Thermal Insulation Performance Test

According to the national standard GB/T10297-2015, the QTM-500 thermal conductivity tester is used for testing. The plate size is 5cm*15cm. The experimental tests tested the thermal conductivity of five sheets of 0, 10%, 20%, 30%, and 40%, as shown in Figure 6.

![Figure 6. Thermal conductivity of five kinds of plates](image)

It can be seen from the above thermal conductivity that the volume fraction from 0 to 20% decreases with the increase of the content of ceramic microspheres. This is because the heat transfer is mainly solid-phase heat conduction, the thermal conductivity of the solid is greater than that of the gas, and the ceramic microspheres are added. Since the interior is hollow, the content of the matrix in the
unit volume of the material is reduced, and the solid content is gradually reduced. The increased spherical pores block the solid-phase heat transfer path, so the introduction of the hollow structure can effectively reduce the thermal conductivity of the composite. The thermal insulation performance of the ceramic microspheres with a content of 20% can easily achieve a better effect, and the microspheres continue to increase and easily break, which in turn affects performance. The thermal conductivity increases after the content of ceramic microspheres is more than 20%, which may be due to the excessive content of ceramic microspheres and the extrusion cracking during compression molding.

4. Conclusion
The anti-insulation integrated material produced can meet the above and more performance to play a role. Increasing the microspheres can reduce the density, heat insulation and slow the ablation. The boron phenolic resin has good ablation resistance, and the quartz fiber has sufficient stability, but the higher the microsphere content, the better. Experimental research shows that the ceramic microspheres the overall performance of the board with 20% and 30% volume fraction is better.

References
[1] Qin Yan, Rao Zhilong, Liu Huijuan, Huang Zhixiong. Study on ablative thermal insulation properties of porcelain phenolic composites [J]. Fiber Reinforced Plastics / Composites, 2012(S1):52-55.
[2] Bahramian A R, Kokabi M, Famili M H N, et al. Ablation and thermal degradation behaviour of a composite based on resol type phenolic resin: process modeling and experimental [J]. Polymer, 2006, 47(10): 3661-3673.
[3] Chen Yongxin, YAO Zhengjun, ZHOU Jintang, et al. Compressive properties and thermal stability of hollow glass microspheres for reinforcing phenolic foams [J]. Journal of Composite Materials, 2014, 31(4): 873-879.
[4] Liying Zhang, J. Ma. Effect of coupling agent on mechanical properties of hollow carbon microsphere/phenolic resin syntactic foam [J]. Composites Science and Technology, 2010, 70(8): 1265-1271.
[5] Gao, Jie; Wang, Jibin; Xu, Haiyan; Wu, Chifei. Preparation and properties of hollow glass bead filled silicone rubber foams with low thermal conductivity [J]. Materials and Design, 2013, 46(2): 491-496.
[6] Chi Huang, Zhixiong Huang, Xuesong Lv, Guangwu Zhang, Qiong Wang, Bo Wang. Surface modification of hollow glass microsphere with different coupling agents for potential applications in phenolic syntactic foams [J]. Journal of Applied Polymer Science, 2017.