Study on Properties of Graphite Polystyrene Permeable Composite Insulation Board

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Abstract. In order to further optimize the properties of polystyrene permeable flame retardant composite insulation board, the composition, properties and flame retardant mechanism of graphite polystyrene permeable flame retardant composite insulation board were discussed in this paper. The properties of graphite polystyrene substrate and permeable flame retardant, the optimum ratio of permeable flame retardant. The tensile strength, compressive strength, thermal conductivity and softening coefficient perpendicular to the plate surface are discussed, and the endothermic flame retardant mechanism of osmotic flame retardant was discussed. The results show that graphite polystyrene permeable flame retardant composite insulation plate does not reduce its combustion and mechanical properties when reduces the density and thermal conductivity.

1. Introduction
With the economic development and social progress, people's awareness of environmental protection has increased, and the sustainable development of building energy conservation has received more and more attention. Polystyrene boards have the characteristics of excellent thermal insulation performance, small bulk density, low thermal conductivity, and convenient construction. It is easy to burn, and generates a lot of harmful gases when burning. Magnesium penetrating flame retardant is a halogen-free green flame retardant, and water and oxides generated during combustion will not cause pollution to the environment; and the flame retardant effect is relatively stable, but magnesium-based penetrating flame retardant and graphite polystyrene insulation board There have been no reports at home and abroad. For this reason, the properties of graphite polystyrene magnesium flame retardant composite panels have been discussed in this paper.
2. Raw materials, experimental equipment and methods

2.1. Raw materials
Graphite polystyrene board and graphite polystyrene permeation flame retardant composite thermal insulation board are produced from the production line of Liaoning Chaoqiang Fireproof Thermal Insulation Technology Co., Ltd., the size is 1000mm × 600mm × 100mm. Magnesium-based penetrating flame retardant: magnesium oxysulfide-based material.

2.2 Experimental methods
Test the basic performance of graphite polystyrene insulation board and inorganic penetrating flame retardant graphite polystyrene composite insulation board according to the national standard "Molded polystyrene board thin plaster external wall insulation system material" GBT29906-2013. According to GB 8624 standard method, the burning performance of graphite polystyrene insulation board and inorganic permeable flame retardant graphite polystyrene (heterogeneous material) composite board was tested.

Optimization of magnesium penetration flame retardant: The molar ratio of magnesium oxide to magnesium sulfate (oxygen-sulfur ratio) is 3:1, 5:1, 7:1, of which 5:1 is added with 30% fly ash, and tested for strength and thermal analysis. The universal surface tensile tester (QL-5E) was used to test the tensile strength of the vertical surface. The intelligent thermal conductivity tester (DRCD-3030) was used to test the thermal conductivity. The high-precision rivet puller (MD60), the test calorific value uses the building material product combustion calorific value measuring device (JCRZ), the test flammability uses the building material non-combustibility experimental device (JCBR), the test temperature uses the infrared thermometer (AS882), and observes its microscopic morphology using scanning Electron microscope (S-4800).

3. Graphite polystyrene board
According to the method described above, the density of the graphite polystyrene board was 18 kg/m³, the thermal conductivity was 0.030, the tensile strength perpendicular to the plate surface was 0.06 MPa. The flammability of graphite polystyrene has been tested to reach B1 level. The TG and DSC curves of the graphite polystyrene board are shown in Fig. 1.

![Fig. 1 TG/ DSC curves of the board](image1)

![Fig. 2 TG / DSC curve of magnesium penetrating flame retardant](image2)

The DSC curve in Fig. 1 shows that the first peak temperature appears at about 314°C, and the heat released is about 193.9 J/g. At the temperature of 484°C, the second exothermic peak of the graphite polystyrene substrate exists. The heat is 164.1 J/g, and the total of the two is about 358 J/g. When the temperature is 374°C, an endothermic peak appears and the heat is 50.64 J/g. It is 307.36 J/g. The TG...
curve shows that the temperature consistent with the starting point of the exothermic peak starts from 291.17°C to 412.72°C, and the mass rapidly decreases from 100% to about 93%. With the second exothermic peak, the mass slowly decreases to 91% and stabilizes. The exotherm of graphite polystyrene board should be the result of the combustion of polystyrene. The heat absorption may be caused by graphite and other flame retardant components.

4. Magnesium penetration flame retardant

Table 1 shows the experimental results of the strength of magnesium infiltration flame retardants with different oxygen-sulfur ratios.

| Oxygen to sulfur ratio | 3:1   | 5:1   | 5:1(Fly ash) | 7:1   |
|------------------------|-------|-------|--------------|-------|
| strength/ MPa          | 55.3  | 58.8  | 62.4         | 60.2  |

Experimental results of strength test based on the different oxygen-sulfur ratio of magnesium penetration flame retardant. With the increase of oxygen-sulfur ratio, the strength of magnesium penetration flame retardant is increased. When the oxygen sulfur ratio is 5:1 and fly ash is added, the highest strength is 62.4MPa. The main reason of high strength when adding fly ash may be that the two main components of magnesium material, magnesium oxide and magnesium sulfate, are the activators of pozzolanic material respectively, which makes the chemical activity of fly ash play a role.

The TG / DSC curve of the optimization of the proportion for magnesium penetration flame retardant is shown in Fig. 2. As can be seen in Fig. 2, there are four endothermic peaks in the DSC temperature curve. The total endothermic area is 2513 J / g, the first endothermic peak temperature is 94°C, the endothermic area is 1228 J / g, and the second endothermic peak The temperature is 434 °C, the endothermic area is 1151J / g, the third endothermic peak temperature is 562 °C, the endothermic area is 109J / g, the fourth endothermic peak temperature is 695 °C, and the endothermic area is 25J / g. The TG curve shows that the mass loss corresponding to the first endothermic peak is about 25%, the mass loss corresponding to the second endothermic peak is about 40%, and the mass loss corresponding to the third and fourth endothermic peaks is about 15%.

Table 2 shows the DSC curve analysis results of magnesium-based penetrating flame retardants with different oxygen-sulfur ratios and optimized ratios.

| Oxygen to sulfur ratio | First   | Second  | Third    | Fourth   | Fifth   | In total Calorific value(J/g) |
|------------------------|---------|---------|----------|----------|--------|-------------------------------|
| 3:1                    | 183/1774| 444/183 | 568/123  | 647/97.85| 0/0    | /2178                         |
| 5:1                    | 174/1664| 442/361 | 566/172  | 640/37   | 704/8  | /2242                         |
| 5:1(Fly ash)           | 163/1639| 441/349 | 556/139  | 644/36   | 709/7  | /2170                         |
| 7:1                    | 160/1378| 438/377 | 564/179  | 624/21   | 704/14 | /1969                         |
| Optimized ratio        | 1228/94 | 1151/424| 109/562  | 25/695   | -      | /2513                         |

Note: temperature (°C )/Calorific value (J/g) of different peaks in table.

Magnesium penetration flame retardant with different oxygen-sulfur ratio and optimized ratio
according to the relevant research of magnesium oxysulfide material\cite{1,2}, it can be concluded that the first endothermic peak is mainly caused by the desquamation of the adsorbed water and the loose binding water from the basic magnesium sulfate material \(x\text{Mg(OH)}_2\cdot\text{MgSO}_4\cdot\gamma\text{H}_2\text{O}\) and magnesium hydroxide \(\text{Mg(OH)}_2\), which will take the heat away. The second, third, fourth and fifth endothermic peaks are mainly caused by the desquamation of the closely bound water.

DSC curves of different oxygen-sulfur ratio and optimized ratio of magnesium penetration flame retardant have similar rules with Fig. 2. There are four or five endothermic peaks at similar temperature, with slightly different calorific value. The change rule of calorific value shows as: the calorific value of 5:1 is greater than 3:1 and 7:1, and the calorific value of 5:1 with a certain amount of fly ash is slightly lower than 5:1 without fly ash, and the maximum calorific value of optimized ratio is 2513 J/g.

According to the relevant research of magnesium oxysulfide material\cite{3,4,5}, the reason for the change of calorific value causes by water and the main crystal phase of the product as \(5\text{Mg(OH)}_2\cdot\text{MgSO}_4\cdot7\text{H}_2\text{O}\) (5:1:7). After adding fly ash, the basic magnesium sulfate with higher water content in the product is replaced by the magnesium silicate (aluminum) hydrate with lower water content due to the chemical excitation of magnesium oxide and magnesium sulfate, which is consistent with the test results of the above strength. The results of comprehensive strength and thermal analysis shows that the optimal one of magnesium penetration flame retardant in different oxygen sulfur-ratio is 5:1.

5. **Graphite polystyrene penetration flame retardant composite insulation board**

Fig.3 is the mechanical properties of the composite plate.

As can be seen in Fig. 3, as the density decreases from 122kg/m\(^3\) to 90kg/m\(^3\), the thermal conductivity of the composite plate decreases from 0.043 w/m.k to 0.037 w/m.k, and the compressive strength decreases from 0.15MPa to 0.10MPa. When the density of the composite plate is increased from 90 kg/m\(^3\) to 100kg/m\(^3\), the tensile strength of the vertical plate surface is increased from 0.10MPa to 0.11MPa, and when the density of the composite plate is increased from 100 kg/m\(^3\) to 122kg/m\(^3\), the vertical plate surface tensile strength is basically constant. Within the test density range, the softening coefficient of the composite board did not change significantly.

The change rule of thermal conductivity and compressive strength conforms to the rule of general composite materials. The change rule for tensile strength of vertical board should be caused by the brittle character of magnesium flame retardant penetrant as the inorganic cementitious materials. The increase of density has limited effected on the improvement of tensile capacity of materials.

The TG/DSC curve of the composite insulation board with the density of 90 Kg/m\(^3\). Produced with graphite polystyrene and the optimized ratio of penetrating flame retardant as the raw material is shown in Fig. 4.
Fig. 4 is visible, the endothermic peaks at 100°C and 150°C exactly match the endothermic peaks in Fig. 2, because the polystyrene has not been fully burned and exothermic at this stage shown in Fig. 1, and the characteristics of the endothermic peaks are determined by the flame retardant. The combustion exothermic peak at about 300°C in Fig. 1 is not obvious due to the influence of the heat absorption of the flame retardant, but the characteristics of the peak temperature still exist. The characteristics of the endothermic peak at about 380°C in Fig. 1 and the endothermic peak at about 420°C in Fig. 2 still exist in Fig. 4, and the endothermic peak at 562°C in Fig. 2 is still obvious, because the exothermic polystyrene has been completed at this stage.

As all known, the mechanism of flame retardancy of combustibles: oxygen, combustibles and ignition point are the three necessary conditions for combustion. Generally, there are three types of flame-retardant mechanisms studied: gas-phase flame-retardant, condensed phase flame-retardant and interruption of heat exchange: (1) Gas-phase flame-retardant mechanism: when the flame retardant is heated, it releases free radicals to interrupt the polymer combustion chain reaction, prevent combustion, release non-combustible gas, dilute the concentration of combustible gas and oxygen around the flame-retardant composite; some flame retardants decompose their own crystal water when heated, it are released in the form of water vapor, which can absorb or take away the heat of polymer surface, to reduce the surrounding temperature and achieve the flame retardant effect.

(2) Condensed phase flame retardant mechanism: it is also known as solid-phase flame retardant mechanism, the flame retardant decomposes into the incombustible substances when heated, and covers the polymer surface to form a protective layer, so as to isolate the outside air and heat from entering into the base material inside, and at the same time prevent the combustible gas inside from escaping, so as to achieve the flame retardant effect; or some flame retardant decomposes and absorbs a lot of heat when heated, which can reduce the surface temperature of polymer and prevent the thermal degradation of polymer. (3) The mechanism of heat exchange interruption: the flame retardant takes a lot of heat away during the combustion of the composite, so as to reduce the surface temperature of the composite and make it lower than the degradation temperature of the polymer, then the material will appear self extinguishing at time.

Through the above analysis, it can be seen that the action mechanism of magnesium permeating flame retardant may be all of the above mechanisms, but the basic characteristics are clear: heat absorption and decomposition dehydration change the atmosphere around the combustibles after heat exposure, and the decomposed non combustibles isolate the oxygen between the combustibles and the environment. In addition, there is no doubt that the matching between the exothermic temperature of polystyrene combustion and the endothermic decomposition temperature of flame retardant is very
SEM analysis of typical interface of graphite polystyrene infiltration composite insulation board is shown in Fig. 5. Shown by the SEM test, the typical characteristics of magnesium permeating and flame retardant materials hydrate of graphite polystyrene permeating composite board are needle-like, sheet-like and needle mesh-like shape, which should be closely related to the water material ratio and process parameters of raw materials. These hydrates are tightly wrapped around the polystyrene particles, that is the structure of inorganic isolation and bin separation is formed when the composite board encounters high temperature in the environment, on the one hand, when the magnesium permeating flame retardant material and polystyrene are in contact with the high temperature environment at the same time, which will be the complex interaction. On the other hand, even if a polystyrene particle burns in the fire and the fire will be blocked, due to the isolation of the magnesium permeating flame retardant material.

Tested by the JCRZ, the heat value of the graphite polystyrene infiltration composite insulation board is about 2.5MJ / kg, which meets the A2 level requirements.

6. Conclusion
1. Graphite polystyrene is used as the substrate, and sulfur-oxygen gelled material is used as the permeation flame retardant. Graphite polystyrene permeation composite insulation boards with a density of less than 100 Kg / m³ and a thermal conductivity of less than 0.04 w / m.k can be prepared.
2. The tensile strength of the plate perpendicular to the surface is 0.1 MPa, the thermal conductivity is 0.039 w / m.k, and the softening coefficient is 0.9.
3. Graphite polystyrene board has Class B1 flame retardant ability, and can be compounded with Magnesium penetrating flame retardant material to achieve Class A2 heat value less than 3MJ / Kg. The flame retardant mechanism of magnesia penetrating flame retardant materials was analyzed as the endothermic flame retardant effect at appropriate temperature.

7. References
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