Optimization of Flame Retardant Amount for Epoxy Anti-Sliding Surface Layer

Jingliang Sheng* and Bin Zhu
Zhong Dian Jian Ji Jiao Expressway Investment and Development Co. LTD
Shijiazhuang 050000

*Corresponding author email: xiaoyu1044@foxmail.com

Abstract. To improve the flame retardant ability of anti-skid epoxy surface material in the tunnel, the paper conducted study on influence of inorganic flame retardant magnesium hydroxide (abbrev. MH), organic flame retardant decabromodiphenylethane (abbrev. DBDPE) and antimony trioxide (abbrev. AO) on the performance after they were applied in anti-skid epoxy surface material. The mechanical properties, rheological properties, combustion properties and thermal stability of epoxy surface with different flame retardants were tested. After optimizing the blending amount to determine the optimal proportion, flame retardant efficiency of those was evaluated. The analysis showed that organic flame retardant DBDPE and AO have a better performance at the same dosage. The oxygen index of DBDPE/AO epoxy cement increased much faster than MH with the amount of flame retardant. When content reached 16%, the oxygen index of the DBDPE/AO reached 31.8%, which meant that it was a flame retardant material and had little effect on other properties of the cement. It is not a good treatment to add too much flame retardant in the epoxy anti-sliding surface, otherwise the rheological properties and mechanical properties would be influenced largely. When the content of composite flame retardant DBDPE/AO got to 12%, each performance index would meet the design requirements. The excessive content of MH was unsuitable because it would greatly reduce the mechanical properties and the ease of construction of epoxy cement. Based on comprehensive performance analysis, 9% DBDPE/AO is recommended as the flame retardant for anti-skid epoxy surface.

Keywords: Pavement engineering, epoxy anti-sliding surface, composite flame retardant, thermal stability, construction and ease of use.

1. Introduction
With the rapid development of the China economy, the scale of infrastructure construction has become larger and larger. As the main material for highway, especially in the tunnel inlet and outlet section, asphalt mixture has some serious performance defects, such as dim color, poor water stability, the mechanical properties, anti-sliding stability and the flame retardant properties and so on [1, 2]. So it is difficult to meet the complex conditions of the tunnel environment. In order to comprehensively improve the driving safety of the Taihangshan expressway tunnel, the paper studied epoxy anti-skid layer paving pavement technology, which isolated the asphalt pavement from the atmosphere, and improved the light reflection coefficient, anti-skid and durability of the pavement in the tunnel. As a high molecular organic material, epoxy resin will undergo oxidative degradation under certain burning conditions outside, generating toxic gases and condensates, which are harmful to the human body[3]. Choosing epoxy anti-sliding, it is necessary to consider how to improve its resistance combustion performance for traffic safety.
In order to improve the flame retardant performance of epoxy anti-skid layer, addition of flame retardant to epoxy cement is usually used to improve the flame retardant performance of the overall material and slow down heat conduction rate to achieve the purpose of flame retardancy, based on epoxy composite. Common flame retardants are organic flame retardants (including bromide, chloride, phosphide, etc.) and inorganic flame retardants (including magnesium hydroxide, aluminum hydroxide, antimony compounds, etc.) [4], among which DBDPE and MH are commonly used. Bromine flame retardants have good compatibility, high flame retardant efficiency and small dosage, but they need to be combined with AO. The relative density of HBr and SbBr₃ generated during the combustion process is very large, which covers the surface of the cement, and of captures active free radicals in the gas states. It reduces the spread of fire and reduces the diffusion of toxic gases[5]. In the process of thermal decomposition, MH will absorb a large amount of heat and generate magnesium oxide to form a dense thermal insulation carbonized layer on the anti-sliding epoxy surface. At the same time, the volatilized water vapor surrounds the flame, blocks the air and dilutes the combustible gas. It is very low and has no secondary pollution. The retardant mechanism of two types belongs to gas phase flame retardant with good flame retardant properties, and they have wide application [6]. There are few researches on the application of flame-retardant epoxy cement for paving roads in China, and it is still in the exploratory stage. Through adding different amounts of DBDPE/AO compound flame retardant and MH to the epoxy cement, the paper will analyze the various performances of modified epoxy cements. And considering the special environment of highway tunnels, the pyrolysis and combustion characteristics of materials are analyzed, and the flame retardancy, mechanical properties, rheological properties are analyzed. Then it will put forward the best balance point between performance and thermal stability, so that all performance indicators can meet the design requirements.

2. Raw Materials and Experimental Program

2.1. Raw Materials
Bisphenol A epoxy resin E44, produced by Yueyang Baling Petrochemical; T-31 curing agent, produced by Zhengzhou Xiangzhida Chemical; C12-14 alkyl glycidyl ether (AGE), produced by Chuzhou Huisheng Electronic Materials Co., Ltd. Quartz sand (0.18mm~0.27mm); flame retardant DBDPE (HT-106), AO (HT-105) and MH (HT-206), processed and produced by Shandong Jinan Taixing Fine Chemical Co., Ltd.

2.2. Experimental Program
The epoxy cement is prepared by melt blending method. According to the results of previous analysis, the dosage of DBDPE/AO compound flame retardant is 0-16%, and the dosage of MH flame retardant is 0-60%. The mechanical properties of the epoxy anti-skid surface binder adopt the static CMT4204 microcomputer-controlled electronic universal testing machine (20kN) of MTS Company; the rheological properties of the binder adopt the MCR-102 dynamic shear flow of Anton Paar Company, Austria The flame retardant performance adopts the IMSYZ2000 oxygen index analyzer supplied by Tianjin British Belle measurement and control equipment; the thermogravimetric analysis adopts the Perkin-Elmer Pyris 1 TGA thermal weight loss analyzer.

3. Performance Characterization

3.1. Mechanical Properties of Flame Retardant Epoxy Binder
The mechanical properties of the flame-retardant epoxy binder were characterized by tensile strength and elongation, tested according to GB/T 1040-2006, the test speed was 5mm/min, and the mass ratio the DBDPE/AO was 3:1[7], and specimen were prepared dumbbell-shaped. The tensile test results were shown in Figure 1.
From Figure 1, it can be seen that the overall tensile strength increases with the increase of single flame retardant content and composite flame retardant, showing a trend of first increasing and then decreasing. When the content of DBDPE and AO are 6.75% and 2.25% respectively, the tensile strength reached the maximum 20.2MPa, which indicating that the flame retardant not only has a flame retardant effect, but also can play a role of filler reinforcement, reduce stress cracking caused by volume shrinkage caused by curing, and improve performance parameters. When the amount of flame retardant was small, the dispersion was more uniform, while the amount was too much, it will cause agglomeration and cracks are easy to appear. The elongation rate of epoxy binder mixed with flame retardant was obviously lower than that of pure epoxy binder. This is because AO is an inorganic powder and has a low thermal expansion coefficient. The addition of DBDPE/AO composite flame retardant will reduce the fracture toughness of oxygen cement. When the amount of flame retardant is less than 10%, the elongation of the epoxy binder meets the requirements of application. Therefore, adding a quantitative composite flame retardant will not have a great impact on the mechanical properties of the epoxy binder. The optimal dosage of DBDPE/AO composite flame retardant is 6%~10%. The tensile strength of epoxy binder mixed with MH ranges from 11.8 to 22Mpa, and the elongation is only 6.5 to 13.5%. The interaction between MH and epoxy binder may increase the overall tensile strength. This is because the inorganic flame retardant MH has poor compatibility with epoxy resin, is not easy to disperse, and has low affinity, which greatly reduces the mechanical properties of the material and loses its flexibility. Therefore, the mechanical properties of the material with flame retardant MH cannot be satisfied after adding this material Requirements.

3.2. Rheological Properties of Flame-retardant Epoxy Binder

During the construction of the anti-skid epoxy surface layer, the rheological properties of the epoxy cement are the key factors affecting the construction workability [8]. The mechanical properties of epoxy cement are improved by adding flame retardant, and the content of flame retardant is adjusted to meet the design requirements. While the addition of flame retardant will change from a homogeneous system to a mixture system, which implies that the flame retardant has the greatest influence on the rheological properties, and the viscosity of the system also increases as the dosage increases. Therefore, the test employed the DSR rheological shear test to study the effect of different amounts of flame retardant on the rheological properties of epoxy resin composites, the test temperature kept staying at 30°C. The test results were shown in Figure 2.
From Figure 2, it can be seen that the flame retardant/epoxy resin composite material is a Newtonian fluid as a whole. A certain amount of flame retardant will not affect the fluid type of the epoxy cement. The DBDPE/AO composite flame retardant and MH solo flame retardant will gradually change the fluid properties of the epoxy resin composite with retardants content increasing. The higher the flame retardant content, the more viscosity of the composite material. That is, the more obvious the pseudoplastic fluid characteristics of the composite material. With the increasing of shear rate, the effect of flame retardant on the viscosity increase of epoxy resin composite is smaller, and the viscosity trend of materials with MH 10% and 20% content is obviously close to that of pure epoxy cement. According to the viscosity curve of the flame retardant/epoxy resin composite material, the nonlinear power function curve is selected as formula (1).

$$\eta = kx^n + b$$  

(1)

The correlation fitting analysis between the amount of flame retardant and the viscosity of epoxy cement is carried out, and the fitting curve is shown in Figure 3.

The fitting curve in Figure 3 shows that the viscosity of the flame-retardant epoxy binder increases gradually with the increase of the content. The viscosity of the MH flame retardant increases significantly when the content is greater than 30%, except for the mechanical properties. The impact will also seriously affect the construction and workability of pavement. It can also be seen that when the DBDPE/AO content is less than 12%, the increasing trend is stable. In order to avoid the excessive viscosity in the construction process that affects the construction efficiency or causes defects such as uneven paving, it is determined that the optimal dosage of DBDPE/AO flame retardant should not exceed 12%, and the optimal dosage of MH flame retardant should not exceed 30%.
3.3. Flame Retardant Properties of Flame Retardant Epoxy Binder

The national standard GB/T2406 method was used to determine oxygen index of epoxy binder materials. The minimum oxygen concentration (LOI) is the oxygen concentration to maintain the combustion of the sample, which is measured in a mixed gas flow of oxygen and nitrogen under normal temperature and normal pressure to test. The combustion performance of modified epoxy cement is studied. LOI is used as the technical index to evaluate the flame retardant performance of epoxy binder. It is generally considered that when LOI<21%, it is flammable; when it is 21%-27%, it is Combustible materials; when it is higher than 27%, it is flame retardant material; when it exceeds 30%, it is flame-retardant material. The strip sample was prepared according to the above specification, the size was 80mm×10mm×4mm, and the test results were shown in Figure 4.

![LOI curve of MH-EP](image1)

![LOI curve of DBDPE/AO-EP](image2)

**Figure 4.** Trend of LOI with flame retardant content.

The test results in Figure 4 showed that the limiting oxygen index increases significantly with the increase of DBDPE/AO content, and a small amount can effectively improve the flame retardant performance of epoxy cement. When the DBDPE/AO content ratio is greater than 9%, the LOI is 27.2%, which is a flame-retardant material; when it is greater than 12%, the LOI is more than 30%, which is a B-I level flame-retardant material with significant flame retardant effect. Compared with pure epoxy, the ignition time increases, and the average heat release rate and flame spread rate are significantly reduced. At the same time, it is better than the best flame retardant effect when MH is used alone. When the amount of MH flame retardant got to 50%, its LOI exceeded 27%, the cementitious material can become a flame retardant material and exerted a flame retardant effect.

4. Conclusion

Through selection DBDPE/AO and MH as representatives of the flame retardants and performance test, the paper studied effect of composite and dosage of flame retardant on epoxy surface performances, and mechanism of flame resistance by the combustion performance test and thermal stability test. The following conclusions were obtained:

1. The addition of DBDPE/Sb2O3 reduces the fracture toughness of the epoxy cement, but it can keep the original physical and mechanical properties better than MH, while significantly improving the tensile strength.

2. The DSR shear rheological curve shows that the optimal amount of DBDPE/AO flame retardant should not exceed 12%, the optimal amount of MH flame retardant should not exceed 30%, and the amount of flame retardant should be too high to cause construction difficulties.

3. The combustion performance of DBDPE/AO flame retardant system is significantly better than that of MH alone, and the oxygen index increases significantly with the increase of DBDPE/AO content, and becomes a flame retardant material when more than 9%.

4. Through systematic analysis of mechanical properties, workability and flame retardancy, it shows that it is advisable to use 9% DBDPE/AO compound as the flame retardant of epoxy anti-skid surface layer with outstanding comprehensive advantages.
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