Effect of ATH / EG Composite Flame Retardant on Properties of High Viscosity Asphalt

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Abstract. In order to improve the flame retardant property of asphalt, ATH (aluminum hydroxide)/ EG (expandable graphite) composite flame retardant was obtained by hydrothermal method. The flame retardancy of asphalt was analyzed by oxygen index test. The rheological properties of asphalt were analyzed by dynamic shear rheological test and bending beam rheological test. The research results show that the optimal mix ratio of the compound flame retardant with the best flame retardant synergistic effect is ATH:EG = 1:1. Considering the flame retardancy and rheological properties, the content of ATH/EG composite flame retardant is recommended to be 15%~20%.

1. Introduction
With the development of highway construction to mountainous and hilly areas, the proportion of highway tunnels increased. As the tunnel environment is closed, it will bring serious harm when the traffic accident causes fire, so the fire safety should be considered in the design [1]. In order to solve this problem effectively, flame retardants have been added to asphalt to improve its flame retardancy performance at home and abroad [2]. Qiu Junlin [3] summarized two aspects of flame retardant performance evaluation criteria and flame retardant technology for tunnels, and finally summarized and proposed five research directions for flame retardant performance of tunnel asphalt pavement in the future. Xin Wei [4] found that there was an interaction between aluminum hydroxide (ATH) and mineral fiber, and the flame retardant efficiency would decrease when the mix dosage of ATH and mineral fiber exceeded a certain critical value, and the LOI index and fiber dosage curve mostly formed an "S" type. Wang Jun [5] synthesized nanoscale magnesium hydroxide (MH) by hydrothermal method, and showed that the LOI index of composite flame retardant asphalt prepared by 8% MH+8% decabromodiphenylethane (DBDPE) reached 29.5%. Tan Yangwei studied [6] the synergistic flame retardation mechanism between kaolin nanotube flame retardants (HNTs) and conventional flame retardants (CFR), and revealed that HNTs/CFR flame retardants are composed of three stages. Xiong Jianping [7] systematically elaborated the flame retardant mechanism of each monomer, compound flame retardant and flame retardant asphalt, and developed DBDPE-Sb2O3 and DBDPE- Sb2O3-ATH two compound flame retardant. Wang Chaohui [8] prepared two new inorganic flame retardants and showed that adding flame retardants can increase the energy required for phase transformation of asphalt and improve its thermal stability. Wei Jiangguo [9] found that DBDPO bromine and ammonium polyphosphate(APP) expansion flame retardants had good flame retardancy and good high and low temperature performance. While ATH flame retardancy and smoke suppression effect were good, but the low temperature crack resistance decreased. Li Ruixia showed [10] that under the synergistic action of warm mix agent and flame retardant, the flame retardant and high-temperature properties of asphalt...
were improved, and the low-temperature crack resistance decreases slightly. In addition, as an intumescent flame retardant, expandable graphite (EG) could significantly improve the flame retardant performance of materials\cite{11}, and were widely used in the fields of chemical plastics, coatings and building fire protection.

To sum up, scholars at home and abroad have successively developed various flame retardants and analyzed their flame retardant mechanism and conducted application research in combination with ordinary dense graded asphalt mixture. However there are few studies on the application of ATH and EG composite flame retardant in pavement. In this paper, ATH / EG composite flame retardant is prepared by hydrothermal method. The composite flame retardant is optimized by limiting oxygen index (LOI), dynamic shear rheology (DSR) and bending beam rheology (BBR).

2. Materials and methods

2.1. Materials

2.1.1. Asphalts

Shell high-viscosity modified asphalt was used in the test design, and the technical indexes of high-viscosity asphalt are shown in table 1.

| Technical Index                      | Units       | Testing Value | Technical Requirements |
|--------------------------------------|-------------|---------------|------------------------|
| Penetration (25℃, 100g, 5s)         | 0.1mm       | 50.1          | ≮40                    |
| Softening Point                      | °C          | 95.7          | ≮80                    |
| Ductility(5 °C)                      | cm          | 38.6          | ≮20                    |
| Brinell Viscosity(135℃)             | Pa·s         | 5.145         | -                      |
| Density (15℃)                       | g·cm⁻³       | 1.032         | -                      |
| Elastic Recovery (25℃)              | %           | 97            | ≮95                    |
| Sticky Toughness (25℃)              | N·m          | 25.6          | ≮20                    |
| Toughness (25℃)                     | N·m          | 16.9          | ≮15                    |
| Rotating Film Heating Test (163℃,85min) | Quality Loss | % | 0.05 | ≮±0.6 |
|                                      | Penetration Ratio | % | 82.1 | ≮±0.6 |
|                                      | Ductility (5cm/min,5℃) | cm | 26.4 | - |

2.1.2. Aluminum hydroxide(ATH)

Aluminum hydroxide (ATH) analytical pure: Aluminum hydroxide content ≥ 99.6%, density 2.4g/cm³, whiteness ≥ 96%, specific area 4 m²/g. ATH flame retardant belongs to additive inorganic flame retardant, non-toxic and non corrosive. Commonly used in industrial production, its flame retardant mechanism is that ATH decomposes and absorbs heat during material combustion, and water evaporation absorbs heat, so as to reduce the surface temperature. In addition, Al₂O₃ produced during decomposition will form a layer of "blanket" wrapped on the material surface to isolate oxygen, reduce the heat transfer of the material, and even have the effect of smoke suppression.

2.1.3 Expandable graphite (EG)

Expandable graphite (EG) industrial products: The purity of expandable graphite is ≥ 96%, the particle size is 80 mesh, and the expansion ratio is > 240 ml/g. EG is an intumescent flame retardant with space lamellar structure. When the conditional temperature is reached, it expands rapidly to increase the layer spacing, and the materials are separated to achieve the flame retardant effect.
2.2. Methods

2.2.1 Limit oxygen index test
Oxygen index (LOI) test is a test that can quantitatively analyze the flammability of materials, as shown in figure 1. This paper uses this test to evaluate the flame retardant performance of asphalt. Using the oxygen index tester, under specific test conditions [12], the minimum O2 concentration when the sample to be tested continues to burn in the mixed gas (O2, N2), and the calculation formula is shown in (1).

\[ \text{LOI} = \frac{O_2}{O_2 + N_2} \times 100\% \quad (1) \]

2.2.2 Dynamic shear rheological test
DSR is a test to describe the rheological properties of asphalt at high temperature, as shown in figure 2. Complex shear modulus G* and phase angle δ can be used to characterize the viscoelastic properties of asphalt. The rheological properties of asphalt at high temperature can be characterized by the rut factor G*/sin(δ). When the G*/sin(δ) of asphalt is not less than 1.0, it meets the specification requirements [13].

2.2.3 Bending Beam Rheological Test
BBR test is a method to accurately evaluate the stiffness and creep rate of asphalt at low temperature, as shown in figure 3. Creep stiffness (S), that is, the resistance of asphalt to permanent deformation; M value is the rate of change of asphalt stiffness under load. The S value of asphalt shall not be greater than 300MPa, and the M value shall not be less than 0.3 to meet the requirements [13].

2.2.4 Synthesis of ATH / EG composite flame retardant
The preparation process of ATH/EG composite flame retardant is shown in figure 4.
First, add an appropriate amount of NaOH into the aqueous solution to provide alkaline environment, then mix ATH and EG in proportion for the first time, add them into the solution, mix them fully, and put them in the reactor (pH=11, T=200°C) for heat preservation for 2h. Finally, after cooling and filtering for 3 times, the product is dried in a 80°C vacuum drying oven to obtain ATH/EG composite flame retardant.

![Figure 4. Preparation process of flame retardant.](image)

The test scheme is shown in table 2. In the design of ATH/EG composite flame retardant ratio, the content of composite flame retardant is 10% of the mass of asphalt, and the ratio is optimized by changing the proportion of ATH: (EG&ATH).

| Test scheme | 1# | 2# | 3# | 4# | 5# |
|-------------|----|----|----|----|----|
| ATH: (ATH&EG) | - | 40% | 50% | 60% | 100% |
| Dosage/% | 10 | 10 | 10 | 10 | 10 |

2.2.5 Preparation of flame retardant asphalt

Heat the high viscosity asphalt to 180 °C, add ATH/EG composite flame retardant after the temperature is stable, use a high-speed shear to shear 700 r·min⁻¹ for 3-5 min until preliminary dispersion, control the rotating speed at 5000 r·min⁻¹ for 35-40 min, then reduce it to 700 r·min⁻¹ for 10min, and finally grow it in a 180 °C oven for 10min to obtain flame retardant asphalt.

The test scheme is shown in table 3. Six kinds of composite flame retardants with different contents are formulated to prepare flame retardant asphalt, and the content of ATH/EG composite flame retardant is optimized.

| Test schemes | 1## | 2## | 3## | 4## | 5## | 6## |
|-------------|-----|-----|-----|-----|-----|-----|
| Dosage (%) | 0 | 5 | 10 | 15 | 20 | 25 |
3. Analysis of test results of ATH / EG flame retardant asphalt

3.1. Flame retardancy

According to the proportion design test in table 2, the oxygen index test results of flame retardant asphalt schemes 1#, 2#, 3#, 4#, 5# are shown in figure 5.

LOI ≤ 22% flammable, 22% < LOI ≤ 27% flammable, 27% < LOI nonflammable. It can be seen from figure 5 that 1# it is pure high viscosity asphalt without composite flame retardant, 1# it is combustible material, and the LOI of other schemes is 22% ~ 27%. 3# LOI reached 24.2, an increase of 3.4 compared with 1# and the LOI was the largest under the condition of 3# the same dosage of flame retardant, so the scheme 3# is selected to further determine the optimal dosage of flame retardant.

The test is designed according to the ratio in table 3, and the oxygen index test results are shown in figure 6.

It can be seen from figure 6 that the flame retardant performance of ATH / EG composite flame retardant asphalt is positively correlated with the content of flame retardant. When the content of ATH / EG composite flame retardant is less than 5%, the flame retardant asphalt is flammable material, and the flame retardant effect is not significantly improved. When the content of composite flame retardant is higher than 5%, the flame retardant effect is significantly improved, and when it is higher than 10%, the LOI of flame retardant asphalt is 24.2%, higher than 23%, meeting the requirements of road asphalt. When the content of flame retardant is 25%, the LOI index of flame retardant asphalt reaches 28.3%, which is 7.5% higher than that of pure high viscosity asphalt, with an increase of 36.0%.

3.2. Rheological properties

3.2.1. Dynamic shear rheological test

The change rule of anti-rut factor (G*/sin(δ)) of flame retardant high-viscosity modified asphalt is shown in figure 7.
Figure 7. The change tendency of asphalt G*sin(δ)

It can be seen from Figure 7(a). G*sin(δ) of asphalt decreases with the increase of temperature under different dosage. When the temperature is between 58°C and 70°C, the G*sin(δ) of asphalt decreases greatly with the increase of temperature gradient. When the temperature is between 70°C and 88°C, the G*sin(δ) of asphalt decreases gently with the increase of temperature gradient.

It can be seen from figure 7(b). The G*sin(δ) of asphalt increases with the increase of dosage at different temperatures. When the dosage of flame retardant is lower than 20%, the G*sin(δ) of asphalt increases gently with the increase of the dosage. When the temperature is higher than 76°C and the dosage increases from 20% to 25%, the G*sin(δ) of asphalt increases obviously with the increase of the content. When the temperature is lower than 76°C and the dosage goes from 20% to 25%, the G*sin(δ) of asphalt increases more significantly with the increase of the dosage. It is shown that adding ATH/EG composite flame retardant can improve the deformation resistance of asphalt, and its high temperature performance can be improved. The polarity of high viscosity asphalt is stronger than that of matrix asphalt. There is a certain compatibility and adsorption between ATH powder and high-viscosity asphalt and EG has excellent compatibility and strong dispersibility. By hydrothermal method, ATH powder is attached to the surface of EG, which greatly improves the compatibility and dispersibility of ATH powder and enhances its adsorption on asphalt, and thus reduces the surface tension between them. The addition of composite flame retardant enhances the anti-flow ability of asphalt, that is, the high-temperature performance of asphalt is improved.

3.2.2. bending Beam rheological test
The creep stiffness (S) and creep rate (m) of flame retardant high-viscosity modified asphalt are shown in figure 8.
Figure 8. The change tendency of asphalt S value and m value

According to figure 8(a) and figure 8(b), when the temperature is -24 °C, the creep stiffness (S) of asphalt is greater than 300MPa, which does not meet the specification requirements. Considering the actual road environment, the analysis is not carried out when the temperature is -24 °C. Creep stiffness (S) increases with the increase of the dosage of flame retardant. When the temperature is -6 °C, the creep stiffness (S) conforms to the specification requirements. When the temperature is -12 °C and the dosage of flame retardant is more than 20%, creep stiffness (S) does not meet the specification requirements.

According to figure 8(c) and figure 8(d), similar to creep stiffness (S), when the temperature is -24 °C, the M value of asphalt is less than 0.3 and does not meet the specification requirements. Considering the actual road environment, the analysis is not carried out when the temperature is -24 °C. The Value of M decreases with the increase of the content of flame retardant. When the temperature is -6 °C, it meets the specification requirements. When the temperature is -12 °C the dosage of flame retardant is more than 20%, the value of M does not meet the specification requirements. There is a certain correlation between creep stiffness (S) and creep change rate (m). Two parameters, creep stiffness (S) and creep rate (m), were considered comprehensively at low temperature. The results show that the addition of compound flame retardant can affect the low temperature performance of asphalt to a certain extent, and it can meet the requirements when the content is controlled within a certain range.

4. Conclusion
(1) When ATH: EG = 1:1, the flame retardant effect of ATH / EG composite flame retardant is the best, and the flame retardant synergistic efficiency of ATH and EG is higher.

(2) When the content of ATH / EG composite flame retardant is 25%, the LOI index reaches 28.3%. Considering the flame retardant and rheological properties of asphalt, the recommended content is 15% ~ 20%.

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