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Flame retardancy, thermal, and mechanical properties of mixed flame retardant modified epoxy asphalt binders

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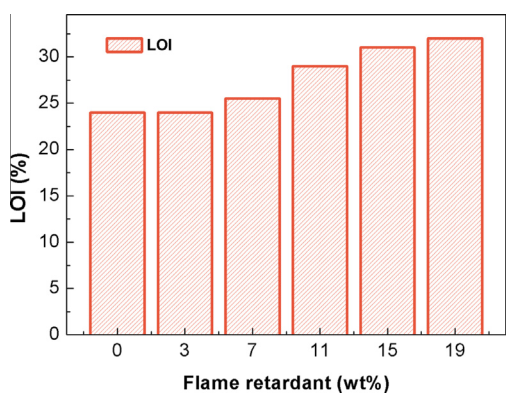
HIGHLIGHTS

- Flame-retarded epoxy asphalt binder is developed.
- The flame retardancy of epoxy asphalt is significantly increased.
- The addition of flame retardants improves the thermal stability of epoxy asphalt binders.
- The presence of flame retardants does not adversely affect the mechanical properties of epoxy asphalt binder.

GRAPHICAL ABSTRACT



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ABSTRACT

The epoxy asphalt (EA) binder has been widely used for the pavement on the steel plate deck and in tunnels. In this study, horizontal burning and limiting oxygen index (LOI) were conducted to evaluate the effects of mixed decabrombromodiphenyl ethane (DBDPE) and antimony trioxide (Sb_2O_3) on flame retardancy for epoxy asphalt binder. The influence of DBDPE/Sb_2O_3 on the rotational viscosity, the thermal and mechanical properties of epoxy asphalt binder was evaluated by thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), and tensile test. The addition of DBDPE/Sb_2O_3 reduces the horizontal burning classification of epoxy asphalt binder from FH-2 to FH-1, and the LOI values of EAs is also significantly increased. The addition of flame retardants has no significant effect on the rotational viscosity of EA in the initial stage of cure reaction. TG results show that the presence of DBDPE/Sb_2O_3 improves the thermal stability of the epoxy asphalt binder. The addition of DBDPE/Sb_2O_3 has little effect on the tensile strength of the epoxy asphalt binder. However, the elongation at break of flame-retarded EAs is lower than that of the neat EA.

1. Introduction

Along with the progress of the society, the highway construction has stepped into the stage of rapid development. Asphalt

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pavement has been becoming the main type of highway paving engineering instead of concrete pavement especially in tunnels [1–3]. However, as an important low-cost thermoplastic, asphalt is flammable. During the combustion, thermal decomposition of asphalt leads to the formation of relatively large amounts of combustible volatile products, which subsequently mix with the surrounding air and burn in the gas phase above asphalt concretes. In order to improve the flame retardancy of asphalt concretes, especially paved in tunnels, flame retardants were often added into the asphalt binders [4–11].

An epoxy asphalt mixture is a polymer concrete made from epoxy resin modified asphalt (epoxy asphalt) binder that is mixed with aggregates. The epoxy asphalt binder is a two-phase thermosetting system in which the continuous phase is a hardener cured epoxy resin and the discontinuous phase is a mixture of specialized asphalts, which makes the mixture's performance different from traditional asphalt mixtures. The cured epoxy asphalt mixture has high strength and toughness, good temperature stability, fatigue resistance and durability, with the advantages of low noise, convenience of maintenance, good skid resistance [12–15]. In the late 1950s, the epoxy asphalt started being used as a material designed to withstand the damage jet fuel, which could damage the pavements. Afterward, epoxy asphalt began to use on the pavement of steel plate decks. At present, the epoxy asphalt is being widely used for not only the pavement on the steel plate deck but also the pavement in tunnels, the pavement at intersections of heavy duty roads, porous asphalt pavements with high durability, colored porous asphalt pavements and so on [16–18]. However, the epoxy asphalt is also quite flammable owing to it is a complex mixture of organic molecules, and it also can produce much smoke and poisonous gases when it is burning. So, it is dangerous to apply epoxy asphalt in tunnels and gas stations. As a result, how to improve the flame retardancy performance of epoxy asphalt has been an event of primary important.

So far, reducing the flammability of asphalt by adding both organic and inorganic additive flame retardants has become a common and effective method [19–24]. And it is well known that halogen-containing fire-retardant chemicals are widely used to improve the fire retardancy of many polymer materials, such as decabromodiphenyl oxide (DBDPO), it is excellent for its bromine amount and thermal stability, but the researcher has suggested that DBDPO can release the toxic and carcinogenic gases of polybrominated dibenzo-p-dioxine (PBDD) and polybrominated dibenzofuranes (PBDF) [25]. Fortunately, decabrombromodiphenyl ethane (DBDPE) can be applied to replace DBDPO because it is equivalent with DBDPO in the bromine amount, thermal stability and molecular mass without releasing PBDD and PBDF during combustion [26].

In this work, DBDPE was used in combination with antimony trioxide (Sb_2O_3) to improve the flame retardancy of epoxy asphalt. The interaction between DBDPE and Sb_2O_3 will produce antimony tribromide ($SbBr_3$) that is a more efficient flame inhibitor than the hydrogen bromide alone in the reaction [27]. Limiting oxygen index (LOI), horizontal burning, thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), and tensile test were used to evaluate the effects of DBDPE/Sb_2O_3 on the flame retardancy, thermal stability, glass transition temperature (T_g) and mechanical properties of epoxy asphalt binders.

2. Experimental

2.1. Materials

Base asphalt (AH-90 paving asphalt) was obtained from China Offshore Bitumen (Taizhou) Co., Ltd. (Taizhou, China). Diglycidyl ether of bisphenol A (DGEBA) was supplied by Wuxi Resin Factory (Wuxi, China), which epoxy equivalent weight (EEW) is 196 g/eq. Modified fatty acids (NDB2) prepared in our laboratory were used as a curing agent. γ-aminopropyltriethoxysilane (APTES) as a silane coupling agent was supplied by the Trustchem Silanes Co., Ltd. (Nanjing, China). DBDPE, with a Br content of 81.5% and an average size of 5 μm was supplied by Shandong Runke Co., Ltd. (Shangdong, China). Sb_2O_3 with particle size of 4–6 μm was manufactured by Shanghai Fourth Solvent Company (Shanghai, China). The mass proportion between DBDPE and Sb_2O_3 was 3:1.

2.2. Samples preparation

NDB2, asphalt, DBDPE, and Sb_2O_3 were mixed using JM-5 colloid mill at 120 °C. Then a certain amount of mixture, APTES, and epoxy resin were stirred at 2000 rpm for 3 min in a 200 mL beaker. After the mechanical agitation, the mixtures were immediately poured into polytetrafluoroethylene (PTFE) molds and cured for 4 h at 120 °C. The mass ratio among epoxy resin, NDB2, and asphalt was 1:2.65:3.25. The DBDPE/Sb_2O_3 (FR) in EA composites was 0, 3, 7, 11, 15, and 19 weight percent of epoxy asphalt binders, respectively.

2.3. Tests and measurements

2.3.1. Limiting oxygen index

LOI are widely used to characterize the flame retardancy of materials and to investigate the effectiveness of flame retardants. In this study, the LOI values were measured on a HC-2C oxygen index instrument (Shangyuan Analytical Instruments Co., Ltd., Nanjing, China) according to ASTM D2863. The samples were molded to the proper size (80 mm × 10 mm × 4 mm). The test procedures were as following: the sample was fixed vertically in the combustion cylinder and was flowed by the mixture of oxygen and nitrogen from the bottom, the top of the sample was ignited by a butane gas flame, recorded the time and length of the combustion, then the minimum oxygen concentration just to maintain a stable combustion can be determined.

2.3.2. Horizontal burning

The horizontal burning test was used to determine the relative rate of burning of epoxy asphalt binders according to ASTM D635 with CZF-4 type instrument (Nanjing Shangyuan Analytical Instruments Co., Ltd., Nanjing, China). The samples were made to a size of 123 mm × 13 mm × 3 mm. In the horizontal burning test, the sample was oriented horizontally and placed in a test chamber, then ignited the end of the sample applied a flame from a Bunsen Burner for 30 s, the time until the flame extinguished itself and the distance the burn propagated must be measured, then figured out the linear burning rate in mm per minute.

2.3.3. Rotational viscosity

Brookfield rational viscometer (Model NDJ-1C, Shanghai Changji Instrument Co., Ltd., China) was used to evaluate the difference in viscous behavior between EA and flame retarded-EAs referring to ASTM D4402. The rotational viscosity tests were conducted at 120 °C.

2.3.4. Thermogravimetric analysis

TG was performed using a Pyris 1 TG analyzer (Perkin–Elmer, USA) to study the thermal stability of epoxy asphalt binders. The test was carried out at a heating rate of 20 °C/min under a nitrogen flow of 40 mL/min with a temperature range of 25 °C to 700 °C.

2.3.5. Glass transition temperature

T_gs of the samples were tested by Perkin–Elmer Pyris 1 DSC (Boston, MA, USA) at heating rate of 20 °C/min in the temperature range from −50 °C to 100 °C under argon at a flow rate of 20 mL/min. DSC results were presented as curves of heat flow versus temperature, in which T_g was defined as the inflection point in the second heating cycle.

2.3.6. Mechanical properties

Following the ASTM D638 method, the Instron computer-controlled mechanical tester (Model 4466, Norwood, MA, USA) was used to measure the tensile strength and elongation at break of the neat EA and flame retarded-EAs. By using thin films, about 2 mm, of the previous conditioned samples, the measurements were conducted with a 500 mm/min crosshead speed at room temperature. Six measurements were taken for each sample and the data were averaged to obtain a mean value.

3. Results and discussion

3.1. Flammability

3.1.1. Horizontal burning

The horizontal burning test is widely applied to evaluate the extent and the linear burning rate of the combustion [28]. The