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.

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 decabromodiphenyl ethane (DBDPE) and antimony trioxide (Sb2O3) on flame retardancy for epoxy asphalt binder. The influence of DBDPE/Sb2O3 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/Sb2O3 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/Sb2O3 improves the thermal stability of the epoxy asphalt binder. The addition of DBDPE/Sb2O3 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
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, decabromodiphenyl 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 (Sb2O3) to improve the flame retardancy of epoxy asphalt. The interaction between DBDPE and Sb2O3 will produce antimony tribromide (SbBr3) 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/Sb2O3 on the flame retardancy, thermal stability, glass transition temperature (Tg) 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. (Shandong, China). Sb2O3 with particle size of 4–6 μm was manufactured by Shanghai Fourth Solvent Company (Shanghai, China). The mass proportion between DBDPE and Sb2O3 was 3:1.

2.2. Samples preparation

NDB2, asphalt, DBDPE, and Sb2O3 were mixed using PM-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/Sb2O3 (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

Tg 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 Tg 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
experimental results of the horizontal burning tests are given in Table 1. From Table 1, it can be seen that the horizontal burning classification of the neat epoxy resin (EP) is FH-3–9.3 mm/min, which is higher than that of the neat EA (FH-2–26 mm). This indicates that the addition of asphalt improve the flame retardancy of epoxy resin. The horizontal burning classification of EA substantially decreased from FH-2 to FH-1 by the addition of only 3 wt% DBDPE/Sb2O3. It reveals that DBDPE/Sb2O3 plays an important role of flame retardant when the epoxy asphalts burn and only a small content of the mixed flame retardants can upgrade the horizontal burning classification of EAs from FH-2 to FH-1, which indicates that the incorporation of DBDPE/Sb2O3 can effectively retard asphalt combustion at a low filling level. Similar results were also reported in the decabromodiphenyl ether/Sb2O3 flame-retarded asphalt binders [5].

3.1.2. Limiting oxygen index

The LOI values of the EP and flame-retarded EAs are shown in Table 1. The LOI of the neat EP is 23.0%. As the DBDPE/Sb2O3 content is increased from 0 wt% to 19 wt%, the LOI increases from 24.0% to 32.0%. These results indicate that the mixed flame retardant modified epoxy asphalt exhibits better flame retardancy than that of the neat EP and the neat EA. Furthermore, the variety of DBDPE/Sb2O3 content has an obvious effect on the flame retardancy for the epoxy asphalt binder. With 11 wt% DBDPE/Sb2O3, the LOI of EA is 29%, which has excellent flame retardancy.

3.2. Rotational viscosity

Unlike thermoplastic asphalt, epoxy asphalt is a thermosetting material, which means that epoxy asphalt’s rotational viscosity will increase during the cure reaction. Therefore, the mixing time should be carefully controlled to give a uniform coating of epoxy asphalt to all aggregates. According to Strategic Highway Research Program (SHRP) specifications, rotational viscosity should be below 3 Pa s for compacting concrete. If the rotational viscosity of EA exceeds 3 Pa s, the concrete becomes very hard to compact the pavement, and eventually it becomes difficult to form an eligible pavement surface [6]. The rotational viscosity–time curves of neat EA and flame retarded-EAs at 120 °C are shown in Fig. 1. For neat EA, the time to 3 Pa s is 70 min. The time to 3 Pa s for the flame retarded EAs is around 65–69 min. Therefore, the addition of flame retardants has no significant effect on the rotational viscosity of EA in the initial stage of cure reaction.

3.3. Thermogravimetric study

TG was used to characterize the influence of asphalt on the thermal stability of epoxy resin. TG and DTG curves of neat EP, base asphalt, neat EA, and DBDPE/Sb2O3 are shown in Fig. 2a and b, respectively. In agreement with the observations of Yu et al. [29], the pyrolysis of the neat epoxy resin can be divided into two stages, as shown in Fig. 2b. First, the weaker chemical bonds are broken and some small gaseous molecules are produced. The temperature range of this stage is from 250 to 400 °C. Second, larger molecules decompose into smaller molecules in the gas phase and coke remains [30,31], which temperature range is from 400 to 550 °C. The acid-cured epoxy resin undergoes the degradation mainly as a two-stage process. The neat EP exhibits a short stage of degradation around 325 °C with an approximately 15% mass loss. This is attributed to the breaking of unreacted epoxy or other traces of impurities apart from the cured epoxy resin. The main degradation takes place above 400 °C and is due to the thermal degradation of the epoxy network [32,33]. The thermal decomposition of epoxy asphalt also contains two stages due to the coexistence of epoxy resin and asphalts. The thermal degradation of DBDPE/Sb2O3 divide into three stages, which are is around 425 °C, 465 °C, and 582 °C respectively.

Table 1

<table>
<thead>
<tr>
<th>DBDPE/Sb2O3 (wt%)</th>
<th>Horizontal burning classification</th>
<th>LOI (%)</th>
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<tbody>
<tr>
<td>EP</td>
<td>FH-3–9.3 mm/min</td>
<td>23.0</td>
</tr>
<tr>
<td>0</td>
<td>FH-2–26 mm</td>
<td>24.0</td>
</tr>
<tr>
<td>3</td>
<td>FH-1</td>
<td>24.0</td>
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<tr>
<td>7</td>
<td>FH-1</td>
<td>25.5</td>
</tr>
<tr>
<td>11</td>
<td>FH-1</td>
<td>29.0</td>
</tr>
<tr>
<td>15</td>
<td>FH-1</td>
<td>31.0</td>
</tr>
<tr>
<td>19</td>
<td>FH-1</td>
<td>32.0</td>
</tr>
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</table>
The initial decomposition temperature (IDT) and temperature of the maximum rate of degradation (T\textsubscript{max}) can be used to ascertain a material lifetime [34]. IDT is assumed to the temperature of 5% mass loss. The IDTs, T\textsubscript{max}s, and residues at 600 °C of the neat asphalt, EP, neat EA, and FR are summarized in Table 2. The IDT and T\textsubscript{max} of EA are slightly greater than that of the neat EP and much lower than that of base asphalt, indicates that the inclusion of asphalts has little effect on the IDT and T\textsubscript{max} of cured epoxy. But the residues at 600 °C of epoxy asphalt are much higher than that of cured epoxy and similar to the base asphalt, since base asphalt contains high residue at the end of thermal decomposition [35].

Fig. 3 shows the TG and DTG curves of EAs with different DBDPE/Sb\textsubscript{2}O\textsubscript{3} contents. The thermal decomposition of EA with 3 wt% flame retardant also occurs in two distinct phases. However, with more flame retardants, the thermal decomposition of EAs becomes to three stages, attributes to the influence of DBDPE/Sb\textsubscript{2}O\textsubscript{3}. The first stage is characterized by a continue mass loss due to the volatilization of the lightest components of asphalts, such as saturates and apolar aromatics, and the breaking of unreacted epoxy or other traces of impurities apart from the cured epoxy as mentioned above, which ends when temperature reaches 340 °C. The second stage covers the range of 350–510 °C and shows the highest value of mass loss rate. During this second step, one peak is observe in DTG curves, as shown in Fig. 3b, due to the decomposition of larger asphalt molecules, the epoxy network, and the flame retardant. Finally, there is a third stage, which basically ends at around 570 °C, which can be mainly ascribed to the thermal decomposition of the flame retardants. The IDTs, T\textsubscript{max}S, and residues at 600 °C of the flame-retarded EAs are summarized in Table 3. It can be seen that the IDT of the flame-retarded EA is slightly higher than that of the neat EA. Furthermore, the T\textsubscript{max} in

![Fig. 4. DSC curves of cured EAs with different DBDPE/Sb\textsubscript{2}O\textsubscript{3} contents.](image1)

![Fig. 5. Tensile strength (a) and elongation at break (b) of EAs with different DBDPE/Sb\textsubscript{2}O\textsubscript{3} contents.](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT (°C)</th>
<th>T\textsubscript{max} (°C)</th>
<th>T\textsubscript{2max} (°C)</th>
<th>T\textsubscript{3max} (°C)</th>
<th>Char at 600 °C (%)</th>
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<tbody>
<tr>
<td>Neat asphalt</td>
<td>326</td>
<td>355</td>
<td>470</td>
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<tr>
<td>EP</td>
<td>299</td>
<td>329</td>
<td>452</td>
<td>–</td>
<td>7.4</td>
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<td>Neat EA</td>
<td>302</td>
<td>318</td>
<td>453</td>
<td>–</td>
<td>16.1</td>
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<td>DBDPE/Sb\textsubscript{2}O\textsubscript{3}</td>
<td>372</td>
<td>426</td>
<td>466</td>
<td>580</td>
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<tr>
<th>Sample</th>
<th>IDT (°C)</th>
<th>T\textsubscript{max} (°C)</th>
<th>T\textsubscript{2max} (°C)</th>
<th>T\textsubscript{3max} (°C)</th>
<th>Char at 600 °C (%)</th>
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<tr>
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<td>318</td>
<td>453</td>
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<td>16.1</td>
</tr>
<tr>
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<td>361</td>
<td>467</td>
<td>–</td>
<td>15.3</td>
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<td>454</td>
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<td>451</td>
<td>548</td>
<td>16.3</td>
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<tr>
<td>19</td>
<td>310</td>
<td>339</td>
<td>478</td>
<td>533</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 2: TGA and DTG results for the neat asphalt, EP, neat EA, and DBDPE/Sb\textsubscript{2}O\textsubscript{3}.

Table 3: TGA and DTG results for EAs with different DBDPE/Sb\textsubscript{2}O\textsubscript{3} contents.
the first stage \((T_{\text{max}}^1)\) and in the second stage \((T_{\text{max}}^2)\) of the flame-retarded EA are greater than those of the neat EA. The \(T_{\text{max}}^2\) of flame-retarded EAs decreases with the increase of DBDPE/Sb\(_2\)O\(_3\) contents, attributes to the \(T_{\text{max}}\) of flame retardant is higher than that of the neat EA, as shown in Fig. 2b. These results suggest that the addition of DBDPE/Sb\(_2\)O\(_3\) improves the thermal stability of the neat EA.

3.4. Glass transition temperature

The DSC curves of the neat and flame-retarded EAs are presented in Fig. 4. It can be seen that the \(T_g\) of the neat EA is 18 °C, which is similar to our previous work [35]. Furthermore, the addition of flame retardants has no significant effect on the \(T_g\) of EAs. There are two competitive factors affecting the \(T_g\), i.e., rigid phase reinforcement and destroying of the epoxy network [36–42]. Therefore, it indicates that the incorporation of DBDPE/Sb\(_2\)O\(_3\) nearly has no effect on the epoxy networks.

3.5. Mechanical properties

Fig. 5 shows the tensile strength and elongation at break of EAs as a function of DBDPE/Sb\(_2\)O\(_3\) content. It can be seen that the neat EA has the maximum tensile strength and elongation at break (toughness), which is 3.35 MPa and 537%, respectively. The addition of flame retardants has little effect on the tensile strength of EAs. The tensile strength of flame-retarded EAs is slightly lower than that of the neat EA. However, the elongation at break of flame-retarded EAs is lower than that of the neat EA. This indicates that the addition of DBDPE/Sb\(_2\)O\(_3\) decreases the toughness of the neat EA. It is worthy to note that even the lowest elongation at break (262%) at 15 wt% DBDPE/Sb\(_2\)O\(_3\) content is much higher than the technical requirement, which is 200%. Therefore, the presence of DBDPE/Sb\(_2\)O\(_3\) does not adversely affect the original mechanical properties of epoxy asphalt binder.

4. Conclusions

On the basis of the results of the effects of mixed flame retardants on the flame retardancy, thermal stability, glass transition temperature, and mechanical properties of epoxy asphalts, the following conclusions can be drawn.

(a) The presence of DBDPE/Sb\(_2\)O\(_3\) decreases the horizontal burning classification of epoxy asphalt binder from FH-2 to FH-1 and the LOI of epoxy asphalt binder also increases significantly. Mixed flame retardants can reduce significantly the flammability of the epoxy asphalt binder at low content.

(b) The addition of flame retardants has no significant effect on the rotational viscosity of EA in the initial stage of cure reaction.

(c) The thermal decomposition of epoxy asphalt binder is affected by the presence of DBDPE/Sb\(_2\)O\(_3\). The two-staged degradation of epoxy asphalt binder changes to three-staged with the addition of DBDPE/Sb\(_2\)O\(_3\). The presence of DBDPE/Sb\(_2\)O\(_3\) improves the thermal stability of epoxy asphalt binders.

(d) The addition of DBDPE/Sb\(_2\)O\(_3\) has no significant effect on the \(T_g\) of epoxy asphalt binders.

(e) It is concluded that DBDPE/Sb\(_2\)O\(_3\) can be employed as a kind of flame retardant for epoxy asphalt binder, without adversely affecting the original mechanical properties of epoxy asphalt binder. Thus, it may provide a newer and safer road material, especially for use in tunnel pavements.

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