Construction and Building Materials 173 (2018) 209–219

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effects of flame retardants on thermal decomposition of SARA fractions separated from asphalt binder

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HIGHLIGHTS

- Flame retardants are selected based on each component decomposition temperature range.
- Flame retardants show obvious improvement on the thermal stability of each component.
- Superposed and densified charring layer inhibits the release of flammable volatiles.
- Composite flame retardant has flame retarding and smoke suppressing synergic effects.
- Matched flame retardants effectively inhibit thermal decomposition of four components.

ARTICLE INFO

Article history:
Received 9 August 2017
Received in revised form 18 January 2018
Accepted 6 April 2018
Available online 24 April 2018

Keywords:
SARA fractions
Flame retardant
Thermal decomposition
Released volatiles
Thermal stability
Combustion residues

ABSTRACT

To better understand effects of flame retardants on thermal decomposition of saturates, aromatics, resins and asphaltenes (SARA) fractions in asphalt binder, different flame retardants were selected to match the thermal decomposition temperature range of each SARA fraction, respectively. Then inhibitory effects of matched flame retardants were discussed and microscopic morphology of combustion residues were observed. The results indicate that the decomposition process of each SARA fraction still includes two thermal mass loss stages after adding the matched flame retardants. However, the thermal decomposition rates are lowered, and the initial decomposition temperatures and maximum decomposition temperatures of each SARA fraction are elevated. Also, the matched flame retardants have few effects on the volatile constituents of four SARA fractions, but show an obvious influence on the release amount of gaseous products. CO_2 and H_2O are still the two main products of each SARA fraction after adding matched flame retardants. Few chemical reactions between SARA fractions and flame retardants are found during their decomposition. Additionally, the superposed and densified charring layers are formed due to the synergic effects of the composite flame retardants. The thick charring layer prevents the heat from transferring, and hinders the oxygen supply, and inhibits the release of flammable volatiles. Finally, the thermal stability of each SARA fraction is greatly improved by the matched flame retardants. The composite flame retardants show a synergistic flame retarding and smoke suppressing effects. This study is beneficial to develop new composite flame retardants for asphalt binder with a satisfactory flaming retarding and smoke suppressing effects.

1. Introduction

Asphalt pavement is widely used in road tunnels due to such advantages as driving comfort, low noise, satisfactory skid resistance, short construction period, maintenance convenience, etc [1]. However, the traffic accidents in the tunnel usually lead to a fire, and a lot of toxic smokes and heat are released because asphalt materials are combustible at a temperature of 300 °C [2]. The released heat and toxic smokes significantly hinder personnel escape and rescue work in tunnels. Therefore, it is necessary to improve the flame retardancy of asphalt binder when exposed to high temperature.

To inhibit the thermal decomposition of asphalt materials, flame retardants were extensively added into the asphalt binder [2]. Currently, different halogen-based flame retardants were used to modify asphalt binder, but this type of flame retardants usually caused severe environmental problems [3]. Therefore, the inorganic halogen-free flame retardants were paid more attention, for example, aluminium hydroxide (ATH), magnesium hydroxide

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https://doi.org/10.1016/j.conbuildmat.2018.04.052
0950-0618/

(MH), calcium carbonate ($CaCO_3$), expandable graphite (EG), hydrated lime (HL) and so on [4]. Some researchers discussed effects of the above environment friendly flame retardants on the thermal decomposition of asphalt binder.

Wu et al. [5] reported the flame retarding mechanism of hydrated lime on asphalt mortar. Zhang et al. [6] analyzed the effects of mixed decabrominated diphenyl ethane and antimony trioxide on the flame retardancy of epoxy asphalt binder. Li et al. [7] discussed the combined effects of flame retardants and warm mixture asphalt additive on pavement performances of asphalt binder. Bonati et al. [4] evaluated the combined effect of clay and conventional flame retardant fillers of ATH and MH on the decomposition process of asphalt mixtures. Xu et al. [8] investigated the influence of magnesium hydroxide (MH) on the volatile release during asphalt combustion.

Simultaneously, the thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) combined technique has been used to evaluate thermal decomposition of polymeric materials. Yan et al. [9] used this technique to discuss the thermal degradation behaviors and flame retarding mechanisms of polyacrylonitrile fibers modified with diethylenetriamine and zinc ions. Chen et al. [10] studied the thermal degradation of flame retarded polyurethane foams based on TG–FTIR tests. Also, the release behaviors of volatiles during the thermal degradation were often examined using TG–DTG-FTIR technique [11]. TG-FTIR technique has become one of main methods to study the thermal decomposition of polymeric materials.

The existing studies showed that the addition of different flame retardants did dramatically inhibit the thermal decomposition of asphalt binder. The research results mentioned above provided a basis to investigate the thermal decomposition of asphalt binder containing different flame retardants. It is well known that asphalt binder, as a kind of multi-component polymeric materials, is usually divided into such four fractions as saturates, aromatics, resins and asphaltenes (SARA) [12]. Further, the thermal decomposition properties and temperature range of each SARA fraction are much different. Thus the thermal decomposition process of asphalt binder shows obvious multistage performance.

However, the constituents of currently used flame retardants are single, which can only play a effective flame retarding role in a certain decomposition stage of asphalt binder. Also, a few studies investigated the inhibitory action of flame retardants on the thermal decomposition of asphalt binder at the component level. Furthermore, the special flame retardants were not selected to match the thermal decomposition temperature range of each SARA fraction during asphalt binder combustion, respectively. This leaded to the decrease in flame retarding efficiency.

In our previous study [13], we have discussed the thermal decomposition of each SARA fraction. It was found that the thermal decomposition temperature range of each SARA fraction showed an obvious gradient distribution characteristic from low to high temperature. This provided a basis to select matched flame retardants for each SARA fraction according to its different decomposition temperature range. As a result, there was a corresponding flame retardant to inhibit the thermal decomposition of each SARA fraction when it is exposed to high temperature.

In this study, different halogen-free flame retardants were first selected to match the thermal decomposition temperature range of each SARA fraction, respectively. Then inhibitory effects of matched flame retardants on thermal decomposition and volatile release of each SARA fraction were discussed based on TG-FTIR tests. Additionally, the constituents and release amount of gaseous volatiles from each SARA fraction in their different decomposition stages were compared before and after adding flame retardants, respectively. Finally, the microscopic morphology characteristics of combustion residues of each SARA fraction were observed using the field emission scanning electron microscopy (FESEM) to further understand the inhibitory properties of matched flame retardants on each SARA fraction. It is believed that the thermal decomposition of asphalt binder is effectively retarded at the component level, which is beneficial to develop an efficient composite flame retardant for asphalt binder. Thus the flame retardancy of asphalt binder is greatly improved, leading to the decrease in released heat and toxic smokes.

Therefore, the objective of this study is to select the halogen-free flame retardants for matching the thermal decomposition temperature range of each SARA fraction. It can inhibit the thermal decomposition of each SARA fraction in their different decomposition stages, and decrease the release amount of heat and toxic volatiles. Further, the effects of matched flame retardants on thermal decomposition and volatile release of each SARA fraction are understood to develop new composite halogen-free flame retardants.

2. Experimental

2.1. Materials

2.1.1. Selection of flame retardants for each SARA fraction

In this study, SARA fractions were separated from asphalt binder according to the standard ASTM D4124-09. The first step was to separate the asphaltenes by n-heptane precipitation. This was done by blending typically 12 g of asphalt binder in 1.2 L of n-heptane and then cooling to the ambient temperature after stirring for 1 h near the boiling point of n-heptane at 98 °C for recovering the insoluble part. The deasphalted asphalt was maltenes. Secondly, the 10 g of maltenes dissolved in 50 mL of n-heptane were passed through a chromatographic column containing CG-20 chromatographic grade alumina. Saturates were first separated using n-heptane as an eluant. Then, pure toluene followed by a blend 50/50 with methanol was used to separate aromatics. Finally, the trichloroethylene was used to separate resins. The contents of saturates, aromatics, resins and asphaltenes were 10.2%, 36.0%, 36.1% and 17.1% (by wt%), respectively. To select the flame retardants for each SARA fraction, the thermal decomposition temperature ranges of SARA fractions were summarized in Table 1 based on the TG test results in air [13].

Flame retardants were physically mixed with each SARA fraction in this study. Therefore, the selection of flame retardants not only took the compatibility into account with each SARA fraction, but also considered the influence of the addition of flame retardants on the conventional pavement performance of asphalt binder and its mixture. In addition, the application of environmentally friendly halogen-free flame retardants has become an inevitable trend because of their advantages of low toxicity, smoke suppression, and environmental protection.

According to the TG-DTG test results of each SARA fraction and the relevant previous studies [14–16], five environmentally

Table 1
TG test results of each SARA fraction in air.

SARA fractions	Temperature range of combustion (°C)	Temperature of maximum weight loss rate (°C)	Mass loss rate (%)
Saturates	228–472	349	88
	472–570	539	12
Aromatics	270–515	400	68
	515–675	600	32
Resins	358–518	457	49
	518–670	590	46
Asphaltenes	375–492	451	31
	492–660	563	57.5