

Pyrolysis Properties and Kinetic Model of an Asphalt Binder Containing a Flame Retardant

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ABSTRACT: In this study, thermogravimetry (TG) experiments were employed to study the influence of magnesium hydroxide (MH) on the pyrolysis characteristics of an asphalt binder. Pyrolysis models of the asphalt binder were developed to reveal the flame-retarding mechanism of MH. The TG experimental results showed that the pyrolysis process of the asphalt binder in N₂ was a one-stage reaction. The asphalt binder containing MH had a higher residue yield ratio at a high temperature, and TG and differential TG curves showed a dramatic shift toward higher temperatures with an increase in the MH concentration; this indicated that MH inhibited the thermal decomposition of the asphalt binder. By optimal identification of the pyrolysis mechanism function, the pyrolysis reaction of the asphalt binder was found to follow the

model of one-dimensional diffusion (parabolic law), whereas that of the flame-retarding asphalt binder followed the model of three-dimensional diffusion (the Ginstling–Brounshtein equation). On the basis of the models, the calculation results for the pseudo activation energy indicated that the thermal stability of the asphalt binder in the pyrolysis process was obviously improved by the addition of MH. We conclude that the flame retardancy of asphalt binders can be enhanced by the use of MH, and MH may be a potential flame retardant for asphalt binders used in tunnel asphalt pavement. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2661–2665, 2011

Key words: activation energy; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Tunnels are integrated components in expressway construction. Because of the many advantages of asphalt pavement, such as driving comfort and safety, low noise levels, fast construction, and easy maintenance, asphalt pavement is becoming widely applied in large-scale road tunnels. However, an asphalt binder is a natural polymer of low molecular weight;¹ its pyrolysis and combustion in a tunnel fire easily lead to plenty of poisonous smoke and toxic gases, which can prevent escape and rescue work. Therefore, the fire retardancy of tunnel asphalt pavement is increasingly a concern.^{2–4}

Because of the flammability of asphalt binders, additives are extensively used to improve their thermal stability. So far, halogen-based flame retardants have been widely employed for this purpose, but halogen-containing materials cause environmental and health problems because of the corrosiveness and toxicity of their combustion products.^{5–7} These

also result in the formation of poisons and plenty of smoke and corrosive fumes during asphalt-pavement construction and tunnel fires. Simultaneously, the technology used to mix flame retardants is complicated during asphalt-pavement construction. This leads to inconveniences in asphalt-pavement construction and increases in cost.

As people's awareness of environmental protection and safety concerns grows, researchers will tend to develop flame retardants that are halogen-free, nontoxic, and smoke-suppressive. Much attention has been paid to halogen-free flame retardants in the past 2 decades.^{8,9} Most halogen-free formulations are based on inorganic fillers such as magnesium hydroxide (MH) and aluminum hydroxide. MH, a kind of halogen-free flame retardant, has properties of flame retardancy and smoke suppression and does not pollute. MH has come into widespread use as a replacement for traditional halogen-containing additives. Many investigations have concentrated on the use of MH as a flame retardant.^{10,11} Furthermore, the starting decomposition temperature of MH is approximately 320°C. At this temperature, an asphalt binder begins to pyrolyze. Thus, MH can be applied to inhibit temperature increases and thermal decomposition of an asphalt-binder matrix in a timely manner. In addition, the thermogravimetry (TG) technique has been extensively used

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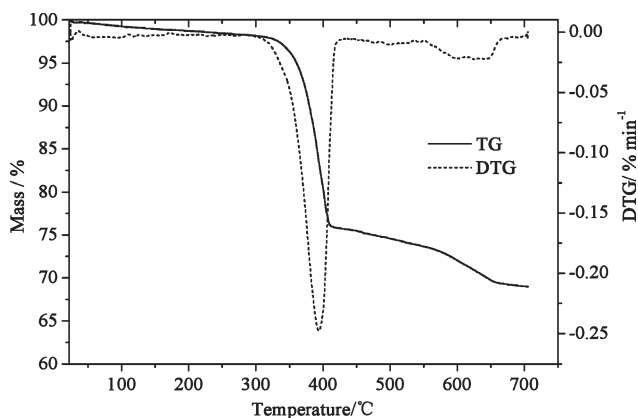


Figure 1 TG-DTG curves of MH.

to study thermal degradation behaviors for many years because it can provide necessary information on the dynamics and thus reveal the combustion mechanism at a low heating rate. Many researchers have employed the experimental results of TG and differential thermogravimetry (DTG) to illuminate increases in the thermal stability of asphalt binders or polymers through the addition of flame retardants.^{12,13} Meanwhile, thermal kinetic analysis has been used to study the pyrolysis mechanisms of different materials.^{14,15} However, this technique is relatively little studied in the field of asphalt pavement.

Even though a lot of work has shown that MH can improve the thermal stability of other polymeric materials, there is less research on MH as a flame retardant of asphalt binders. Moreover, the main study methods have been limited to laboratory-scale testing. Thermal kinetic analysis of flame-retarding asphalt binders has seldom been presented. The pyrolysis kinetic model of asphalt binders, used to reveal the flame-retarding mechanism of flame retardants in binders, is rarely studied.

In this study, TG experiments were used to investigate the effects of MH on the pyrolysis characteristics of an asphalt binder, and a pyrolysis model of the asphalt binder was developed to probe the flame-retarding mechanism of MH in the binder. Also, pyrolysis kinetic parameters were calculated to evaluate quantitatively the flame-retarding effects of MH. It may be helpful to deeply understand the flame-retarding mechanism of a metal hydroxide in an asphalt binder, and this may provide some useful information for flame-retardant formulations.

EXPERIMENTAL

Materials

An asphalt binder modified with styrene butadiene styrene (SBS) was obtained from Shell Bitumen Co., Ltd. (Guangdong, China), with a penetration of 72 dmm at 25°C, a ductility of 36.5 cm at 5°C, a soften-

ing point of 75.5°C, a viscosity of 2.6 Pa s at 135°C, and a flash point of 323°C.

The flame retardant MH was produced by Guangzhou Yaxin Chemical Ltd. Co. (Guangzhou, China). The flame retardant was a white, nontoxic powder with an average particle size of 2.2–3.0 μm , a density of 2.36 g/cm³, and a crystal water content of 31.0%. The pyrolysis performance of MH in N₂ at a heating rate of 10°C/min is shown in Figure 1.

Preparation of the samples of the flame-retarding asphalt binder

The SBS-modified asphalt binder was put into a stainless steel cup to heat on an electric furnace with an asbestos shim. After the asphalt binder was heated to $170 \pm 5^\circ\text{C}$, the flame-retardant powder was added to the hot asphalt binder at weight percentages of 5, 10, 15, 20, and 25%. The asphalt binder was stirred with an FM200 shear machine (Fluko Equipment Co., Ltd., Essen, Nordrhein-Westfalen, Germany) first at $170 \pm 5^\circ\text{C}$ for 15 min, then at a higher speed of 5000 rpm for 30 min, and finally at a lower speed of 500 rpm for 15 min to expel air bubbles. Lastly, the fire-retarding asphalt binder was put into clean vessels. During the process of cooling to room temperature, hand stirring was maintained to prevent segregation.

Measurements

The experiment was conducted with a TGA-92 thermal analyzer system (Setaram Co., Ltd., Lyon, Bouches-Alpes, France). Temperature control and data acquisition were implemented automatically by a computer online. To simulate the pyrolysis behavior of the asphalt binder, TG experiments were conducted in highly purified N₂. The samples were heated from room temperature to 750°C at a heating rate of 10°C/min under an N₂ flow of 60 mL/min. Nonisothermal kinetic experiments were carried out with approximately 10 mg of the MH-modified asphalt binder. Thermal kinetic analysis parameters of the asphalt-binder samples were calculated with the Coats-Redfern method.¹⁶

RESULTS AND DISCUSSION

Influence of MH on the pyrolysis properties of the asphalt binder

To evaluate the effect of MH on the pyrolysis behavior of the asphalt binder, TG experiments with the pure asphalt binder and asphalt-binder/MH composite were performed in N₂. TG and DTG curves with different concentrations of MH are shown in Figure 2.

Figure 2 shows that the weight loss of the asphalt binder started at approximately 280°C, and more than 90% of all weight loss occurred in the range of 300–500°C. Before 320°C, MH did not begin to decompose and absorb heat; the weight losses of the samples were

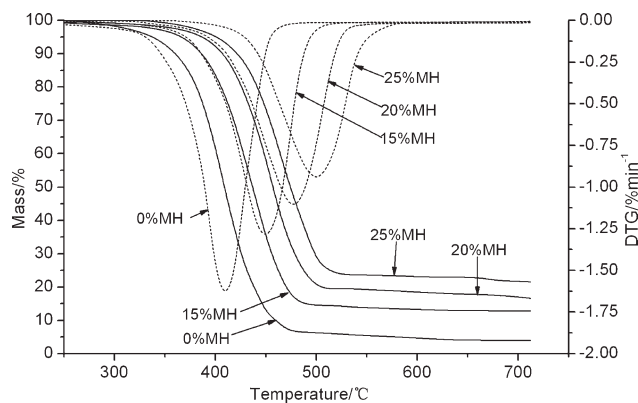


Figure 2 TG–DTG curves of asphalt-binder pyrolysis with different concentrations of MH.

similar. When the samples were heated to 320°C, MH began to decompose. The heat in the asphalt-binder matrix was absorbed because of MH thermal decomposition, so the temperature rise was inhibited. This delayed the release of flammable volatiles from the asphalt-binder matrix. The temperatures at the maximum weight loss rate and at the beginning of pyrolysis (with a 2% weight loss) increased, but the maximum weight loss rate decreased. Meanwhile, the residue yield ratio increased with the MH content rising, and this was propitious for retarding further pyrolysis of the asphalt binder¹⁷ (as shown in Table I). According to Table I, when MH was added to the asphalt binder at concentrations of 15, 20, and 25 wt%, the residue yield ratio increased correspondingly by 57.2, 76.5, and 105.3%, respectively. This was attributed to the active magnesia yielded by MH decomposition, which impelled the asphalt-binder surface to char and formed a charring layer. The layer kept heat away from the asphalt binder and flammable volatiles out of the asphalt-binder matrix; therefore, MH had a flame-retarding effect on the asphalt binder.

In addition, DTG curves of the asphalt/MH composite showed a dramatic shift of approximately 30°C toward higher temperatures. Furthermore, DTG curves of asphalt-binder pyrolysis exhibited obvious unimodal characteristics. This indicated that the pyrolysis process of the asphalt binder was a one-step reaction. Once the temperature was higher than 500°C, the weight loss of the samples was less, and the residue weight changed little. All this indicated that MH improved the thermal stability of the asphalt binder and hindered the release of pyrolysis volatiles at high temperatures. This may be valuable for winning more time for escape and rescue work in tunnel fires.

Pyrolysis model of the asphalt binder

The pyrolysis reaction rate is a function of the heating rate, temperature, and pyrolysis product mass. When a nonisothermal reaction is assumed

to divide into an infinite number of short time periods, the reaction in every single time step is taken to be isothermal. Hence, it is reasonable for the pyrolysis reaction to be described by the Arrhenius law.¹⁸

It is well known that TG and DTG can be used for thermal dynamic analysis.^{19,20} According to the Arrhenius equation, the pyrolysis reaction rate of an asphalt binder can be written as follows:

$$d\alpha/dt = k \cdot f(\alpha) = Ae^{(-E/RT)}f(\alpha) \quad (1)$$

where k is reaction rate constant, A is the pseudo frequency factor or pseudo pre-exponential factor (s^{-1}), E is the pseudo activation energy (kJ/mol), R is the universal gas constant ($kJ\ mol^{-1}\ K^{-1}$), t is the time of the pyrolysis process (s), T is the pyrolysis temperature at time t (K), α is the residue matter mass (kg), and $f(\alpha)$ is the function related to the reaction rate and α .

When a constant heating rate ($\beta = dT/dt$) is assumed, eq. (1) becomes

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} e^{(-E/RT)} dT \quad (2)$$

If we define integral function $g(\alpha)$ as

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha$$

then eq. (2) becomes

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{(-E/RT)} dT \quad (3)$$

where T_0 is the initial temperature.

Some previous studies also used TG curves for thermal dynamic analysis.^{21,22} The Coats–Redfern method was used to solve the kinetic equations in this study. It deduces the approximate integral-type equation and can be described as follows:

TABLE I
Characteristic Temperatures of Asphalt-Binder Pyrolysis and Residue Yield Ratios with Different MH Concentrations

MH concentration (%)	Temperature of 2% weight loss (°C)	Temperature of maximum weight loss rate (°C)	Residue yield ratio (%)
0	302	409	15.53
15	350	449	24.41
20	351	461	27.82
25	354	472	31.88

TABLE II
Common Pyrolysis Mechanism and Integral Mechanism Functions

Pyrolysis mechanism	Symbol	Mechanism function $[g(\alpha)]$
One-dimensional diffusion (parabolic law)	D1	α^2
Two-dimensional diffusion (Valensi equation)	D2	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
Three-dimensional diffusion (Jander equation)	D3	$[1 - (1 - \alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling-Brounshtein equation)	D4	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
One-dimensional phase boundary reaction (Maple powder law)	R1	A
Two-dimensional phase boundary reaction (shrinking column shape symmetry)	R2	$1 - (1 - \alpha)^{1/2}$
Three-dimensional phase boundary reaction (shrinking sphere shape symmetry)	R3	$1 - (1 - \alpha)^{1/3}$
Two-order chemical reaction	F2	$(1 - \alpha)^{-1}$
Three-order chemical reaction	F3	$(1 - \alpha)^{-2}$
Nucleation and nucleus growth (Maple single law, one order)	A1	$-\ln(1 - \alpha)$
Nucleation and nucleus growth (Avrami-Erofeev equation)	A2	$[-\ln(1 - \alpha)]^{2/3}$
Nucleation and nucleus growth (Avrami-Erofeev equation)	A3	$[-\ln(1 - \alpha)]^{1/2}$
Nucleation and nucleus growth (Avrami-Erofeev equation)	A4	$[-\ln(1 - \alpha)]^{1/3}$
Nucleation and nucleus growth (Avrami-Erofeev equation)	A5	$[-\ln(1 - \alpha)]^{1/4}$

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (4)$$

Common integral functions $[g(\alpha)]$ used to study the kinetic analysis are summarized in Table II.^{23–25} As is known, when a kinetic model is applied to describe the pyrolysis reaction of materials, it must be verified by various methods. Kinetic analysis is one of the methods used to verify the rationality of developed models. The degree to which a linear relationship is approached between $\ln[g(\alpha)/T^2]$ and $1/T$ is an evaluation of the developed models.

From eq. (4), because $2RT/E \ll 1$, $2RT/E$ can be neglected. This makes $\ln[AR(1 - 2RT/E)/(\beta E)]$ approximately equal to $\ln(AR/\beta E)$. Therefore, when reaction function $g(\alpha)$ is selected appropriately, the curve of $\ln[g(\alpha)/T^2]$ versus $1/T$ should be approximately a straight line by least-square curve fitting. Obviously, $g(\alpha)$ with the maximum correlation coefficient R^2 is the mechanism function of the pyrolysis reaction. The slope of the regression line is $-E/R$, and the intercept includes A . Therefore, the pseudo-

kinetic parameters (E and A) can be calculated with the slope and intercept of the regression line. Curve-fitting results for the correlation coefficient of the mechanism functions for asphalt-binder pyrolysis with different MH contents are shown in Figure 3.

By optimal identification of the pyrolysis mechanism function (as shown in Figure 3), the reaction of asphalt-binder pyrolysis has been found to agree with D1 in fluid N_2 , that is, the one-dimensional diffusion (parabolic law) model. This shows that the reaction of asphalt-binder pyrolysis belongs to a diffusion-process-controlled mechanism, represents a deceleration-type α - t curve, and follows a parabolic rule.¹⁶ Moreover, the reaction mechanism function of the asphalt binder is $g(\alpha) = \alpha^2$, and the reaction rate function is $f(\alpha) = \alpha^{-1/2}$.

However, the pyrolysis reaction of the flame-retarding asphalt binder follows the D4 model, that is, the three-dimensional diffusion model. This shows that the pyrolysis reaction of the MH-modified asphalt binder also belongs to a diffusion-process-controlled mechanism, but it represents spherical symmetry and a deceleration-type α - t curve and follows the Ginstling-Brounshtein equation.¹⁶ Additionally, the reaction mechanism function of the flame-retardant-modified asphalt binder is $g(\alpha) = (1 - 2\alpha/3) - (1 - \alpha)^{2/3}$, and the reaction rate function is $f(\alpha) = 3/2 [(1 - \alpha)^{-1/3} - 1]^{-1}$.

Analysis of the kinetic parameters of pyrolysis

When the pyrolysis model of the asphalt binder was determined, the pseudo activation energy was estimated, and the calculation results are shown in Table III. When MH was mixed into the asphalt binder, the pseudo activation energy obviously increased with the content of MH increasing. In comparison with the experimental results in Table I, with an increase in the pseudo activation energy, the temperatures corresponding to the initial thermal decomposition and the maximum weight loss rate of the asphalt-binder samples containing various concentrations of MH were also elevated. This indicates that more heat was needed to activate the thermal decomposition reaction with the

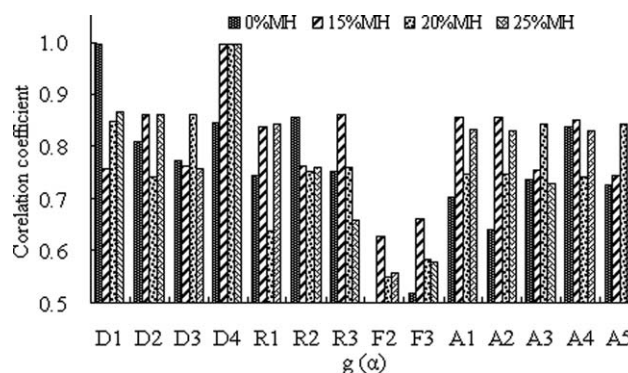


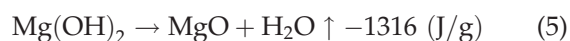
Figure 3 Correlation coefficients of functions for asphalt-binder pyrolysis obtained with different MH concentrations.

TABLE III
Calculation Results for the Pseudo Activation Energy of Asphalt-Binder Pyrolysis in N₂

MH concentration (wt %)	0	15	20	25
Pseudo activation energy (kJ/mol)	96.15	112.12	131.25	149.68

increase in the pseudo activation energy. Therefore, the flame-retarding asphalt binder had a higher pseudo activation energy than the pure asphalt binder. This trend agreed with previous research.¹³ Therefore, compared with the pure asphalt binder, the MH-modified asphalt binder was more difficult to decompose. This was consistent with the TG experiment results.

The main reasons were that MH released crystal water and absorbed heat from the asphalt-binder matrix as MH decomposed; this inhibited the temperature of the binder matrix from rising, decreased the reaction rate, and retarded the pyrolysis reaction of the asphalt binder. When the reaction temperature exceeded 320°C, MH that was dispersed in the asphalt binder decomposed to absorb the heat (ca. 1.316 kJ/g), and this led to the reduction of the temperature. MH decomposes according to the following endothermic reaction:²⁶



On the other hand, active MgO from the MH thermal decomposition impelled the asphalt-binder surface to generate a tight charring layer. The layer was very stable and was a good fire-resistant material: it hindered heat flux in the asphalt matrix and kept volatiles out of the asphalt matrix. The layer hindered further pyrolysis of the asphalt binder, and the reaction of asphalt-binder pyrolysis was effectively inhibited. Therefore, the thermal stability of the flame-retarding asphalt binder was improved, and the goal of flame retardation was achieved.

CONCLUSIONS

The following main conclusions were obtained from the experiment results and discussion:

1. The flame retardant MH could improve the flame retardancy of the asphalt binder effectively. The pyrolysis process of the asphalt binder and asphalt-binder/MH composite was a one-step reaction in N₂. The residue yield ratio of the asphalt binder gradually increased with the concentration of MH increasing. The release of flammable volatiles from the asphalt binder was delayed at high temperatures, and this could help with escape and rescue work.
2. The pyrolysis reaction of the asphalt binder followed the reaction model of one-dimensional dif-

fusion (parabolic law), and its reaction mechanism function was $g(\alpha) = \alpha^2$. However, the pyrolysis reaction of the flame-retardant-modified asphalt binder followed the model of three-dimensional diffusion (the Ginstling–Brounshtein equation), and its reaction mechanism function was written as $g(\alpha) = (1 - 2\alpha/3) - (1 - \alpha)^2/3$.

3. MH had an obvious influence on the kinetic parameter of asphalt-binder pyrolysis. The pseudo activation energy of the flame-retarding asphalt binder in the pyrolysis process was higher than that of the pure asphalt binder, and this indicated that the thermal stability of the asphalt binder was obviously improved by the addition of MH. We conclude that MH is a potential flame retardant for asphalt binders used in tunnel asphalt pavement.

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