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Effect of Particle Size and Content of Magnesium Hydroxide on Flame Retardant Properties of Asphalt

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ABSTRACT: The flame-retardant properties of asphalt for some building applications are very important. This article is mainly focused on the influence of particle size and content of magnesium hydroxide (MH) on the flame-retardant properties of asphalt. The limit oxygen index and cone calorimeter results indicate that as the MH content and mesh number increase, the flame-retardant properties of MH-filled flame-retardant asphalt show a rising trend. But the role of particle size in smoke suppression is not obvious. Several tests confirm that the dispersion of the MH have some influence on the flame-retarding effect of asphalt. The 3000 mesh MH for the preparation of flame-retardant asphalt shows optimal performance. The experimental data show that the softening point of flame-retardant asphalt increases, but the ductility and penetration decrease with increasing MH content. MH affects the asphalt viscosity, but not affects the adhesion of the asphalt to gravel. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2261–2272, 2013

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INTRODUCTION

As a basis for building materials, asphalt is widely used in areas such as road tunnels, underground garages, gas station floors, buildings, and as a waterproof material. The largest area of asphalt use is concrete pavement. Because of such properties as low noise, good slip resistance, easy maintenance, and ride comfort, asphalt has become the main material of road construction. But asphalt is highly flammable and gives out a lot of smoke while burning, hazards that cannot be ignored. Comparing with other commonly used polymers, asphalt is easier to flow after heated to a relative low temperature, which makes the fire spread in a short time. Furthermore, the gases produced during asphalt combustion such as alkanes, benzene, and methylbenzene could not only accelerate the combustion but also cause choking to die. These hazards limit the application of asphalt in tunnel road projects and make it necessary to change the combustion properties of asphalt. The simplest method of preparing flame-retardant asphalt is adding a flame retardant to the asphalt to form a composite. The flame retardants used for asphalt are those commonly used for polymer materials and are studied by using research methods for polymer materials, but there are different ways to examine the combustion characteristic of asphalt.[1] At present, the commonly used organic flame retardants such as halogen and phosphorus flame retardants used in polymer materials are toxic; these flame retardants are often volatile and release toxic irritant gases at high temperatures. These toxic irritant gases are harmful to the health of staff in the asphalt mixing plant, road construction, and in the event of fire. Because of the poor ventilation inside a tunnel, the smoke and toxic gases generated become a serious impediment to the escape and rescue of personnel.[2–4]

Since the 1990s, as the demand for flame-retardant asphalt grows, flame-retardant asphalt research has made a lot of progress. Hageman was granted a patent for the preparation of flame-retardant asphalt linoleum in 1990.[5] In this patent, sodium bicarbonate is added to the asphalt felt to accelerate the curing of it, and surprisingly the asphalt flammability is reduced at the same time, probably because the carbon dioxide resulting from the decomposition of sodium bicarbonate contributes to flame asphyxia. Grube was granted a patent in 1991 for using borate as flame-retardant agent for asphalt.[6] Slusher was issued a patent in 1996 for using expansion flame-retardant agent to modify asphalt.[7] Brown was issued a patent in 2001 for using bauxite, brucite, and other inorganic flame-retardant agents to modify asphalt. According to cone calorimeter (CONE) test results, the effects of these flame-retardant agents were better than that of the traditional inorganic flame-retardant aluminum hydroxide (ATH).[8]

In view of the low smoke and low toxicity requirements of road and tunnel asphalt, new studies on low smoke zero halogen flame-retardant agents for asphalt, such as the hydroxides and salts of magnesium, aluminum, zinc, and boron, have drawn considerable attention. These environmentally friendly flame retardants have the characteristics of low toxicity, smoke suppression, low corrosion, and low cost. But their flame-retardant efficiency is not high, and the flame-retardant effect is not obvious when we use one flame-retardant agent alone. Thermal gravimetric analysis results showed that asphalt mass loss occurs predominantly in the temperature range 250–430°C.[9] ATH whose decomposition temperatures coincide with those of magnesium hydroxide (MH) can broaden the range of decomposition temperatures of the flame retardant, plays a synergistic role in asphalt retardancy, greatly improving the flame-retardant properties.[10] The effect of zinc borate on smoke suppression, promotion of char formation, smoldering inhibition, and droplet prevention has been confirmed. In 2008, Qu[11] used ATH and MH as flame-retardant fillers to effectively improve the softening point of asphalt, but the penetration and ductility were reduced. With increasing content of MH and ATH, the penetration and ductility decreased, but the softening point increased. Adding MH or ATH can improve the asphalt high-temperature resistance to permanent deformation of the asphalt, but destroy intermolecular bonds, reducing the shrinkage resistance of the asphalt. Thermal gravimetric analysis results show that adding MH or ATH can increase the pyrolysis temperature of the asphalt. The active oxide produced by the decomposition of the flame-retardant filler is attached to the surface of the asphalt to prevent droplet formation and suppress smoke.[12] In 2011, Jiang[13] made a new, highly efficient flame-retardant asphalt called ZFR–Ti. This new flame-retardant asphalt uses MH and ATH as the main fillers, with a certain amount of ammonium polyphosphate (APP). Surface activation by a titanium acid ester coupling agent improved the dispersibility and compatibility of the inorganic flame-retardant fillers in the asphalt. In addition to the significant effect on low-temperature ductility of the asphalt, this new flame-retardant system has little effect on other properties such as penetration, softening point, and elastic recovery indicators.

Now production technologies have made it possible to produce a diverse particle size of MH. The particle size of MH has been reported to affect its dispersion in polymer (such as rubber), which has the significant influence on the flame-retardant properties.[14,15] However, comprehensive reports about this research area are few. In this study, we focused on MH particle size and content. Through extensive testing of asphalt filled with MH with different particle sizes and contents, we evaluated the effect of MH on the flame retardant and physical properties of asphalt. We also analyzed the dispersion of MH in asphalt and provided a reference for the future rational design of ATH- and MH-filled flame-retardant asphalt. In addition, we also focused on using CONE to study the flame-retardant properties of asphalt. Now in China, asphalt (AH-70) has been widely used for road pavement in view of its good properties, so in this study, we chose it for our base materials and discussed its flame-retardant properties modified by MH.

EXPERIMENTAL

Materials

The asphalt selected for this study, AH-70, was obtained from the Qinhuangdao Petroleum Petrochemical Company. The flash point of the asphalt is 250°C, the ignition point is 330°C, and the limiting oxygen index (LOI) is 24%.

The various grades of MH with the particle sizes of 1250, 2000, 2500, 3000, and 5000 mesh were provided by Dalian Yatai Science and Technology New Materials Company. For the sake of cost saving and simplicity of analysis, the MH used in this study was not subjected to any surface treatment.

Equipment

Particle size distribution was measured by a Mastersize 2000 laser particle size analyzer produced by Malvern Company, Great Britain. MH particle morphology was observed by an S-4700 scanning electron microscope (SEM) produced by Hitachi Company, Japan. Flame-retardant performance was tested by a JF-606 Oxygen Index instrument and CZF-3 Horizontal and vertical burning instrument produced by Jiangning Analysis Instrument Factory, and an FTTO242 CONE manufactured by FTT Company, Great Britain. An RPA2000 rubber processing analyzer (RPA) manufactured by Alpha Company, USA and an XL-30 environmental SEM (ESEM) were used for dispersion detection. The viscosity of asphalt was measured by a DV-II+ Pro rotational viscometer produced by Brookfield, USA. Other asphalt performance tests were carried out according to Chinese national standards.

Preparation of Experimental Samples

Preparation of Flame-Retardant Asphalt. We first distributed the asphalt into different stainless steel containers to avoid aging caused by repeated heating of the same sample, which may affect the flame-retardant properties of the asphalt. Each stainless steel container was heated in an oven at 110°C for about 20 min to melt the asphalt inside. The container was transferred to an electric heating kit maintained at the constant temperature of 160°C. After the asphalt was heated up to 160 ± 5°C, a given amount of flame retardant (MH) was added to the hot asphalt. The asphalt was stirred by using an FM200 shear machine (FLUKO Equipment Company, Germany) at 160 ± 5°C for 15 min, and then at the high speed of 5000 rpm for 30 min. Different amounts (5, 10, 15, 20, and 30%) and particle sizes (1250, 2000, 2500, 3000, and 5000 mesh) of MH were used to prepare different flame-retardant asphalt samples.

Preparation of Test Samples. The test strips for the horizontal and vertical burning test and limiting oxygen index test and the test slices for the cone calorimeter test were prepared by mold casting.

A cardboard mold approximately 150 mm × 150 mm × 4 mm was used for the test strips for the horizontal and vertical burning test. A ceramic tile platform was capped with a layer of

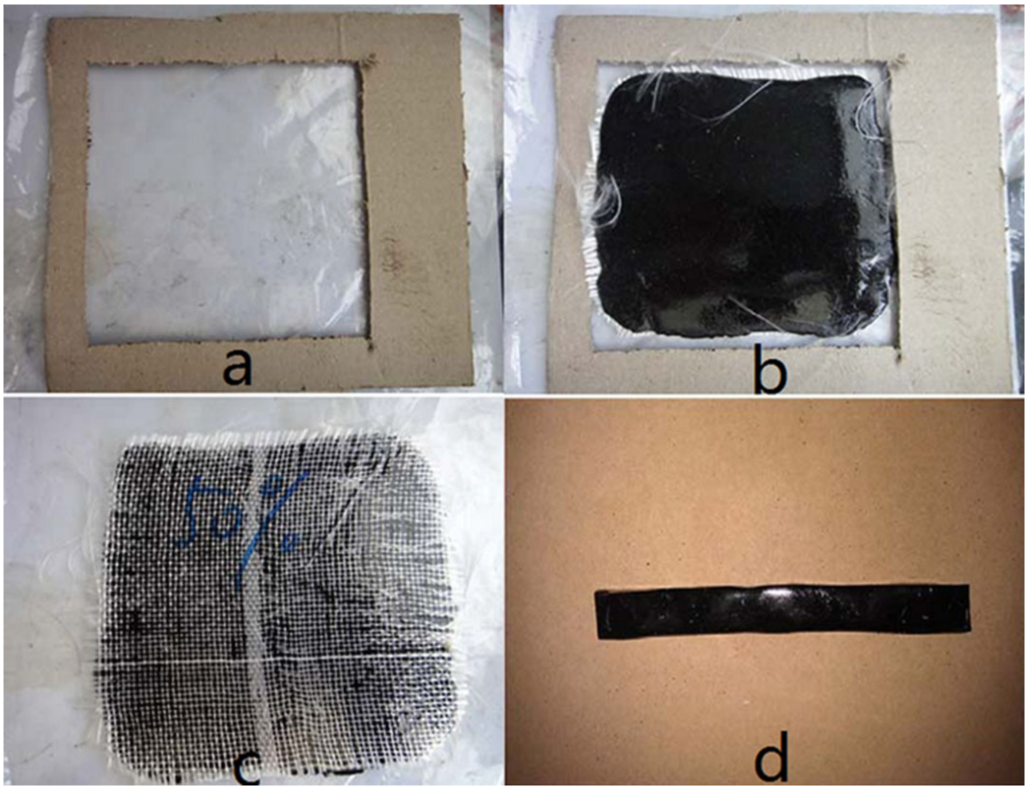

Figure 1. Preparation of test strip for horizontal and vertical burning. (a) cardboard mold; (b) asphalt in mold; (c) back side of asphalt sample; (d) well-cut test strip. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cellophane and then covered with a layer of fiberglass cloth. The mold was put on the fiberglass cloth and the molten flame-retardant asphalt was poured into the mold and cooled to room temperature. The mold was removed from the sample, the bottom cellophane torn off, and the molding cut into a test strip 125 mm long, 13 mm wide, and 3 mm thick. The test strip edges should be cut very smoothly by the scissors. The preparation of the test samples is illustrated in Figure 1.

A test strip for the limiting oxygen index test was made with a detachable copper mold with a cavity 170 mm × 13 mm × 4 mm. After applying a release agent on the mold wall, place the mold wall on the glass fiber cloth and splice them well. Then the mold cavity was filled with a molten asphalt sample at about 160°C and let asphalt cool to room temperature. At last, the mold was withdrawn from the sample slowly and the test strip obtained. Before the test, the strip edges need to be cut carefully and smoothly by the scissors. The strip was further cut along the vertical and horizontal centerlines to form four 85 mm × 6.5 mm × 4 mm strips. The preparation of the test samples is illustrated in Figure 2.

To get test slices meeting cone calorimeter test requirements, we made a mold with a cavity 100 mm × 100 mm × 3 mm. The mold cavity was filled with the molten asphalt at about 160°C to maximum thickness. After the samples cooling to room temperature, demold carefully and keep cryopreservation of the samples. The test slice for cone calorimeter was shown in Figure 3.

Analyses

The horizontal and vertical combustion method is equivalent to the UL-94 test in the United States. We performed the

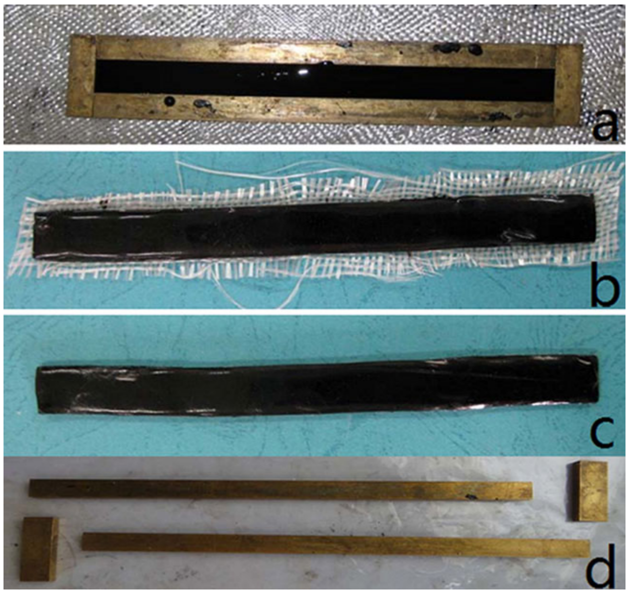

Figure 2. Preparation of test strip for limiting oxygen index. (a) asphalt in mold; (b) untrimmed test strip; (c) well-cut test strip; (d) detachable copper mold. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Preparation of test slice for CONE test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

horizontal and vertical combustion test according to Chinese standard GB/T2408-1996. The limit oxygen index (LOI) was measured according to Chinese standard GB/T2406-2008. Although the asphalt test strip had a glass fiber cloth support, during the combustion process, the asphalt test strip still showed softening deformation, lodging, and dropping phenomenon, and sometimes also jumping fire phenomenon. These phenomena influenced the accuracy of the results. For better accuracy, each test was repeated at least 12–16 times. In the horizontal combustion test, the operator can stabilize the combustion by properly supporting the asphalt test strip with a glass rod. In the vertical combustion and limiting oxygen index tests, we must guarantee that the asphalt test strip is strictly vertical to avoid lodging of test strip during the combustion.

The CONE analyzes flame retardants by measuring oxygen consumption during the fire test, in which the irradiation heat flow is well controlled and maintained. Specimens were wrapped in aluminum foil and placed in the combustion box. External heat flux was set at 50 kW/m^2. Different flame properties of the asphalt were evaluated, such as the time to ignition (TTI), heat release rate (HRR), peak heat release rate (pkHRR), effective heat of combustion (EHC), and specific extinction area (SEA).

The RPA is a dynamic mechanical rheometer that can not only determine the dynamic mechanical properties of rubber, but also detect the filler dispersion. By analyzing the relationship between polymer modulus (G') and strain, we indirectly get the dispersion of the filler in the polymer. We used the same test conditions of 40°C and 400% strain to characterize the dispersion of MH with different particles sizes and contents in the asphalt.

ESEM can be used to observe the dispersion of MH. At the observation temperature, the asphalt samples melt gradually and covering the MH powder, so we need to prepare the sample rapidly in liquid nitrogen and observe the sample immediately.

In accordance with the specification of "*Standard Test Methods of Asphalt and Asphalt Mixture for Highway Engineering*" JTJ 052-2000,[16] we tested measured the viscosity (T0625-2000) of flame-retardant asphalt. The experimental temperature was setting at 135°C. The rotor model for 21S, the speed of rotor was 20 rpm, and the weight of a sample was 8.0–10.0 g.

In accordance with the specification of "*Standard Test Methods of Asphalt and Asphalt Mixture for Highway Engineering*" JTJ 052-2000,[16] we tested the ductility (T0605-1993), penetration (T0604-2000) and softening point (T0606-2000).

Adhesion test used boiled method (T0616-1993) in accordance with the specification "*Standard Test Methods of Asphalt and Asphalt Mixture for Highway Engineering*" JTJ 052-2000.[16] Gravels used in these experiments were muscovite granite.

RESULTS AND DISCUSSION

MH Particle Size and Morphological Characterization

The particle size distribution of MH was measured by a Mastersize 2000 laser particle size analyzer. Test results are shown in Table I. The result shows that there is a certain size distribution. Through data comparison, we can find that various data between 2500 mesh MH and 2000 mesh MH do not differ much, but the big gap between 3000 mesh MH, while 3000 mesh MH and 5000 mesh MH data do not differ much. So there are differences between the number of actual heading and test results.

The SEM images of MH particles are shown in Figure 4. The scaly micron particle in the shape of irregular rod is MH. The lower the mesh number, the larger the particle size. Comparing Figure 4(d) and Figure 4(e), we see few differences between 3000 mesh MH and 5000 mesh MH.

Effect of MH on Asphalt Flame-Retardant Properties

Horizontal and Vertical Combustion. The test results are shown in Table II. It can be seen from Table II that the

Table I. $Mg(OH)_2$ Particle Size Parameters

Samples	Specific surface (Area/m^2/g)	Surface average particle diameter/μm	D(0.1)/μm	D(0.5)/μm	D(0.9)/μm
1250 mesh MH	1.62	3.709	1.770	5.542	17.583
2000 mesh MH	1.93	3.113	1.456	4.755	14.771
2500 mesh MH	1.97	3.051	1.409	4.439	15.656
3000 mesh MH	2.62	2.288	1.179	2.960	6.733
5000 mesh MH	2.65	2.267	1.165	2.925	6.706

Note: D (0.1), D (0.5), and D (0.9) are the most probable particle sizes at 10%, 50%, and 90% of all the particles, respectively.

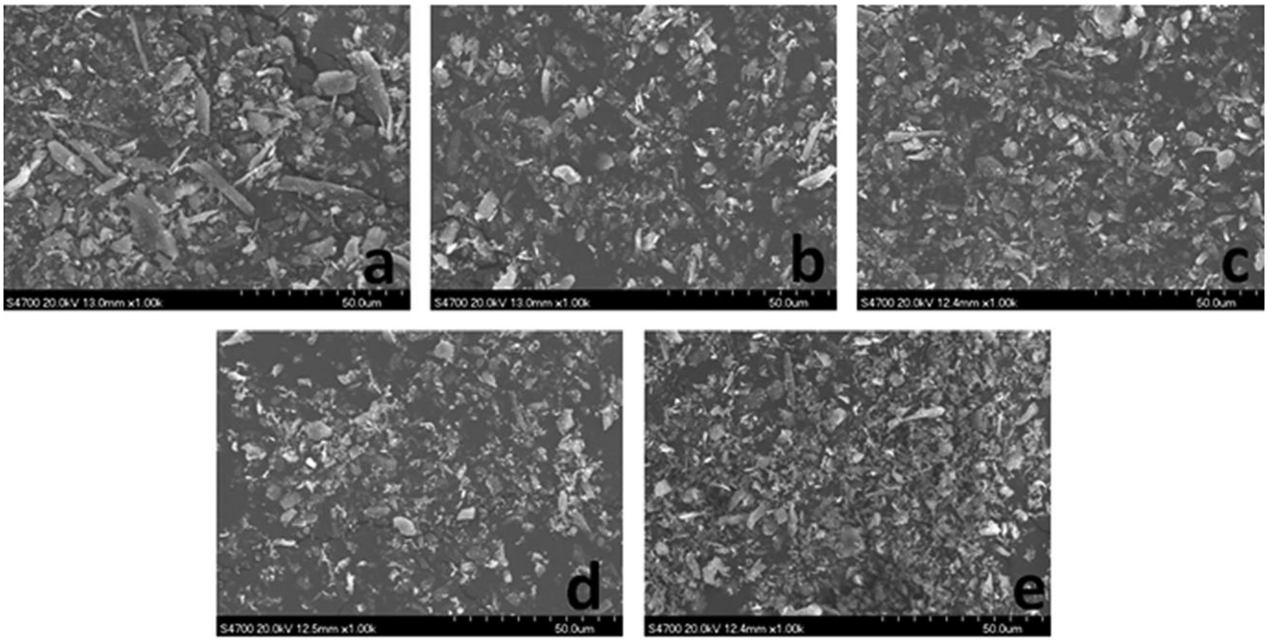

Figure 4. SEM images of MH with different particle sizes. (a) 1250 mesh; (b) 2000 mesh; (c) 2500 mesh; (d) 3000 mesh; (e) 5000 mesh.

horizontal combustion level for pure asphalt is FH-2. Adding 5% of MH to asphalt improves the horizontal combustion level to FH-1, which means that the combustion of the sample does not exceed 25 mm. However, further increases in the MH content have no effect on the horizontal combustion level.

As shown in Table III, the vertical combustion level of pure asphalt is FV-2, while the best vertical combustion level of flame-retardant MH/ asphalt composite is FV-0. The vertical combustion data also confirm the flame-retardant effect of MH. With increasing content of MH, the vertical combustion level increases obviously. For example, when the MH content is 5%, the burning time is about 30 s. As the MH content reaches 15%, the burning time of most samples are shorter than 15 s, even as short as 9 s, meaning the sample basically cannot be ignited. When the MH content reaches 30%, all samples are rated FV-0. Fluctuations of individual data exist because of the difficulties in carrying out the asphalt combustion experiments. Further increases in particle size (increases in mesh number above 2000 mesh) have little influence on vertical combustion performance.

Table II. Horizontal Combustion Results

Pure asphalt	FH-2				
Content of MH/%	5	10	15	20	30
1250 mesh	FH-1	FH-1	FH-1	FH-1	FH-1
2000 mesh	FH-1	FH-1	FH-1	FH-1	FH-1
2500 mesh	FH-1	FH-1	FH-1	FH-1	FH-1
3000 mesh	FH-1	FH-1	FH-1	FH-1	FH-1
5000 mesh	FH-1	FH-1	FH-1	FH-1	FH-1

Note: FH-1: burning no more than 25 mm, FH-2: burning between 25 and 100 mm, FH-3: burning more than 100 mm.

LOI. The results of the limit oxygen index test are shown in Figure 5. The oxygen index OI is calculated as follows:

$$OI = [O_2]/([O_2] + [N_2]) \times 100\% \tag{1}$$

where, $[O_2]$ is the volumetric flow rate of oxygen (L/min) and $[N_2]$ is nitrogen flow (L/min).

When the LOI value of a material is higher than 27%, the material is a self-extinguishing material. According to Japanese standard JISK 7201 requirements, flame-retardant materials are divided into five categories. Flame-retardant materials with LOI values lower than 21% are classified as nonflame-5, which is the least flame-retardant level. Flame-retardant materials with LOI values between 21% and 24% are classified as nonflame-4. Flame-retardant materials with LOI values between 24% and 27% are classified as nonflame-3. Flame-retardant materials with LOI values between 27% and 30% are classified as nonflame-2. Flame-retardant materials with LOI values more than 30% are classified as nonflame-1.[17] The LOI value of pure asphalt is generally between 19% and 22%. Depending on the composition of the asphalt, flame-retardant asphalts with LOI values higher than 27% are possible, but rare.

It can be seen from Figure 5 that the LOI value of flame-retardant asphalt increases with increasing MH content at a given MH particle size, confirming the effect of MH on the flame-retardant properties of the asphalt. At a given MH content, the LOI value increases with decreasing MH particle size up to about 2500 mesh. Further decreases in MH particle size result in no improvement of the LOI value. The LOI values of 5000 mesh MH/asphalt composites are significantly lower than those

Table III. Vertical Combustion Results

Pure Asphalt	FV-2(135 s)				
Content of MH/%	5	10	15	20	30
1250 mesh	FV-2	FV-2	FV-1(16 s)	FV-0(7 s)	FV-0
2000 mesh	FV-2(34.0 s)	FV-1(13.5 s)	FV-0(9.1 s)	FV-1(10.9 s)	FV-0(6.3 s)
2500 mesh	FV-1(13.9 s)	FV-1(12.2 s)	FV-1(13.3 s)	FV-0(6.8 s)	FV-0(8.7 s)
3000 mesh	FV-2(24.1 s)	FV-1(19.7 s)	FV-1(12.7 s)	FV-0(7.9 s)	FV-0(3.0 s)
5000 mesh	FV-2(20.2 s)	FV-2(27.8 s)	FV-0(9.3 s)	FV-2(27.5 s)	FV-0(7.0 s)

Note: FV-0: total burning time shorter than 10 s, FV-1: total burning time between 10 and 30 s, FV-2: total burning time longer than 30 s.

of 3000 mesh MH/asphalt composites and close to those of 2000 mesh MH/asphalt composites. So the particle sizes of the flame retardants used for asphalt are not the finer the better. MH that is too fine is prone to agglomeration in the sticky asphalt, resulting in poor flame-retardant properties of the asphalt. Without surface treatment, MH with particle sizes in the range 2500–3000 mesh is optimum.

CONE. When asphalt is heated by radiation, it melts and eventually ignites. From the intensity of the fire, we can make qualitative judgments on the flame-retardant effect. The residue left in the aluminum foil box shows a thin layer of white oxide film on the surface and a hard black material underneath, as shown in Figure 6.

From the flame-retardant mechanism of MH-filled asphalt, we can determine that the hard black substance consists of carbides of asphalt, and the surface oxide film is magnesium oxide, which prevents oxygen from contacting with asphalt, and resulting in flame-retardancy. Therefore, the addition of MH can achieve flame-retardant purpose by absorbing heat and releasing water of crystallization, the MH can also form an oxide film blocking oxygen and asphalt contact to promote the asphalt to form a carbide layer, inhibition of the asphalt to further combustion. Different from the high viscosity of the other polymers which can keep their original shape even though their viscosity decrease, the asphalt turns to liquid quickly because its viscosity rapidly decreases to a low value with increasing temperature. The oxide particles generated by the decomposition of MH easily aggregate on the surface of the asphalt, forming a magnesium oxide barrier layer.

In the CONE test, the TTI refers to time from the beginning of heating of the surface to the continuous burning of the sample at a given thermal irradiation. The longer the TTI, the better the flame-retardant properties of the material. Tables IV, V, and VI present the TTI results of flame-retardant asphalt filled with

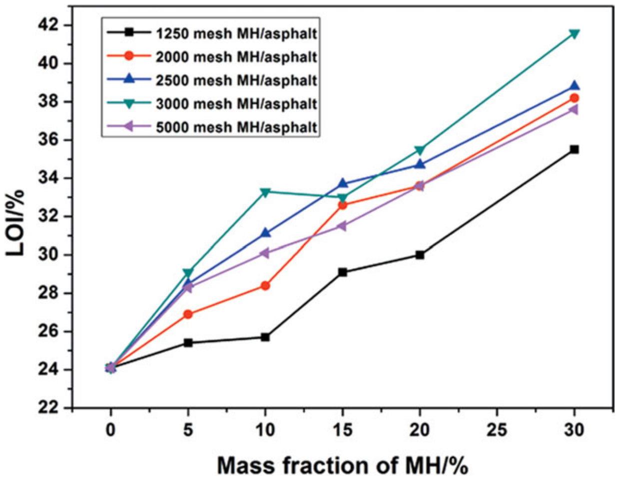

Figure 5. LOI curves of MH-filled flame-retardant asphalt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Image of residue of CONE test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. TTI and pkHRR Results of MH-filled Asphalt at a MH Content of 5% and Different MH Particle Sizes

Samples	TTI(s)	pkHRR (kW/m^2)
Pure asphalt	26	482.1
5% 1250 mesh MH/asphalt	24	370.3
5% 3000 mesh MH/asphalt	32	343.2
5% 5000 mesh MH/asphalt	24	389.7

Table V. TTI and pkHRR Results of MH-filled Asphalt at a MH Content of 30% and Different MH Particle Sizes

Samples	TTI(s)	pkHRR (kW/m^2)
Pure asphalt	26	482.1
30% 1250 mesh MH/asphalt	42	319.7
30% 3000 mesh MH/asphalt	52	321.2
30% 5000 mesh MH/asphalt	42	293.1

MH with different particle sizes and contents. It can be seen that TTI increases with decreasing MH particle size (increasing mesh number) below 3000 mesh. The TTI of flame-retardant asphalt filled with 3000 mesh MH is longer than that of flame-retardant asphalt filled with 5000 mesh MH because the dispersion of 5000 mesh MH is poor. TTI generally increases with increasing MH content except 15% of 3000 mesh MH.

The HRR is a very important indicator of flame-retardant performance. The larger the values of HRR and the pkHRR, the larger the heat release of the material and the greater the fire hazard. The HRR curves are shown in Figure 7. It can be seen from Figure 7(a–c) that the prominent combustion peak for pure asphalt disappears and the HRR remains relatively constant during combustion after the addition of MH because the endothermic decomposition of the MH and the formation of the oxide film during combustion hinder further combustion of the asphalt. As a result, the HRR is reduced. Figure 7(a) shows that late in the combustion process, at a MH content of 5% the HRR of 3000 mesh MH/asphalt are lower than that of 5000 mesh MH/asphalt. At a MH content of 30%, the HRR of 5000 mesh MH/asphalt is the lowest early in the combustion process, while late in the combustion process, the HRR of MH-filled flame-retardant asphalt does not depend on the MH particle size, as shown in Figure 7(b). Comparing Figure 7(a) with Figure 7(b), we can make the conclusion that 3000 mesh MH is more appropriate than the other mesh MH for reducing the values of HRR. Figure 7(c) shows the HRR curves for asphalt filled with different amounts of 3000 mesh MH. In the initial and middle periods of combustion, with increasing content of MH, the effect of MH on reducing the HRR of asphalt is more obvious than late in the combustion process.

The effective EHC is the heat released by the decomposition of the volatiles in the composition during the combustion process. It is also a very significant indicator of flame-retardant performance. The lower the EHC, the better the flame-retardant performance. From Figure 8(a,b), we can see that in the initial burning stage of the MH-filled flame-retardant asphalt, the 3000 mesh MH gives the better flame-retardant performance than the other mesh MH. Figure 8(c) shows the effect of MH

Table VI. TTI and pkHRR Results of Asphalt Filled with Different Amounts of 3000 Mesh MH

Samples	TTI(s)	pkHRR (kW/m^2)
Pure asphalt	26	482.1
5% 3000 mesh MH/asphalt	32	343.2
10% 3000 mesh MH/asphalt	39	367.8
15% 3000 mesh MH/asphalt	28	318.1
30% 3000 mesh MH/asphalt	52	321.2

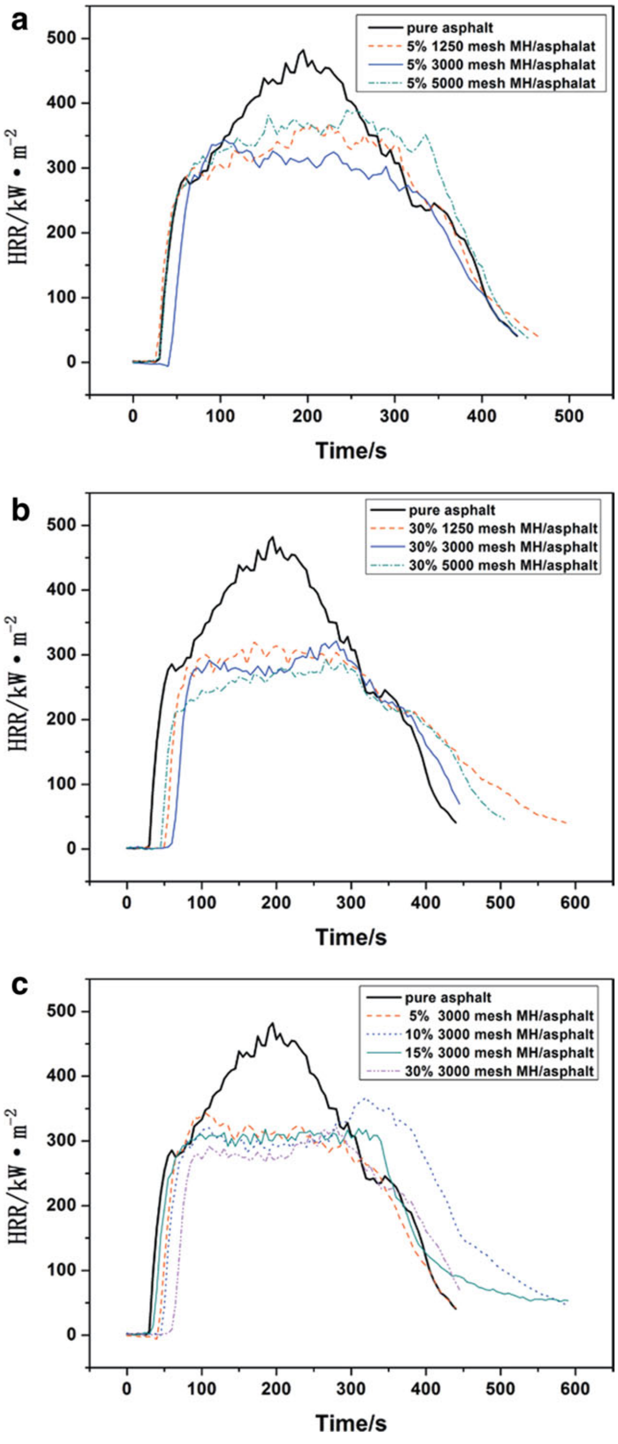

Figure 7. HRR curves of CONE test: (a) HRR curves for MH-filled asphalt at a MH content of 5% and different MH particle sizes; (b) HRR curves for MH-filled asphalt at a MH content of 30% and different MH particle sizes; (c) HRR curves for asphalt filled with different amounts of 3000 mesh MH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content on the EHC of asphalt filled with 3000 mesh MH. In the initial burning stage, a MH content of 30% shows a more significant effect than other content in reducing the EHC. Thus, the selection of MH that disperses well in asphalt will reduce the EHC. As the MH content increases, the reduction in EHC will also increase.

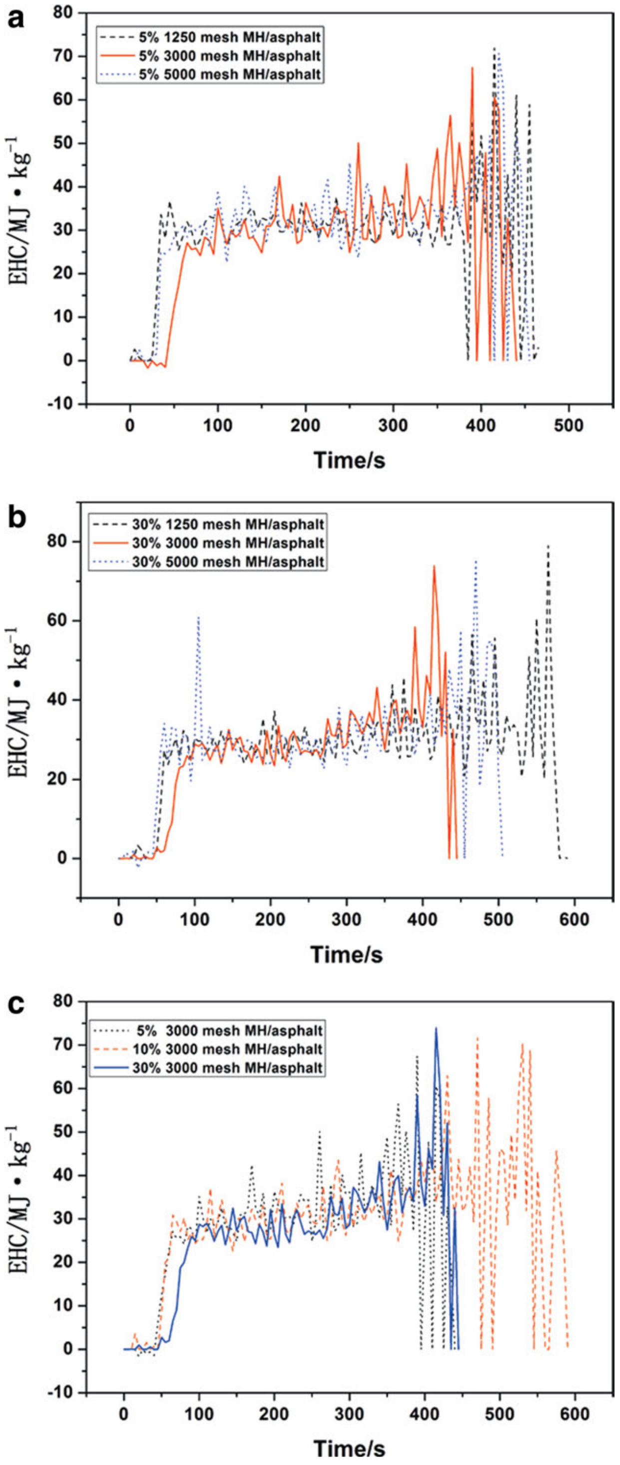

Figure 8. EHC curves of CONE test: (a) EHC curves for MH-filled asphalt at a MH content of 5% and different MH particle sizes; (b) EHC curves for MH-filled asphalt at a MH content of 30% and different MH particle sizes; (c) EHC curves for asphalt filled with different amounts of 3000 mesh MH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

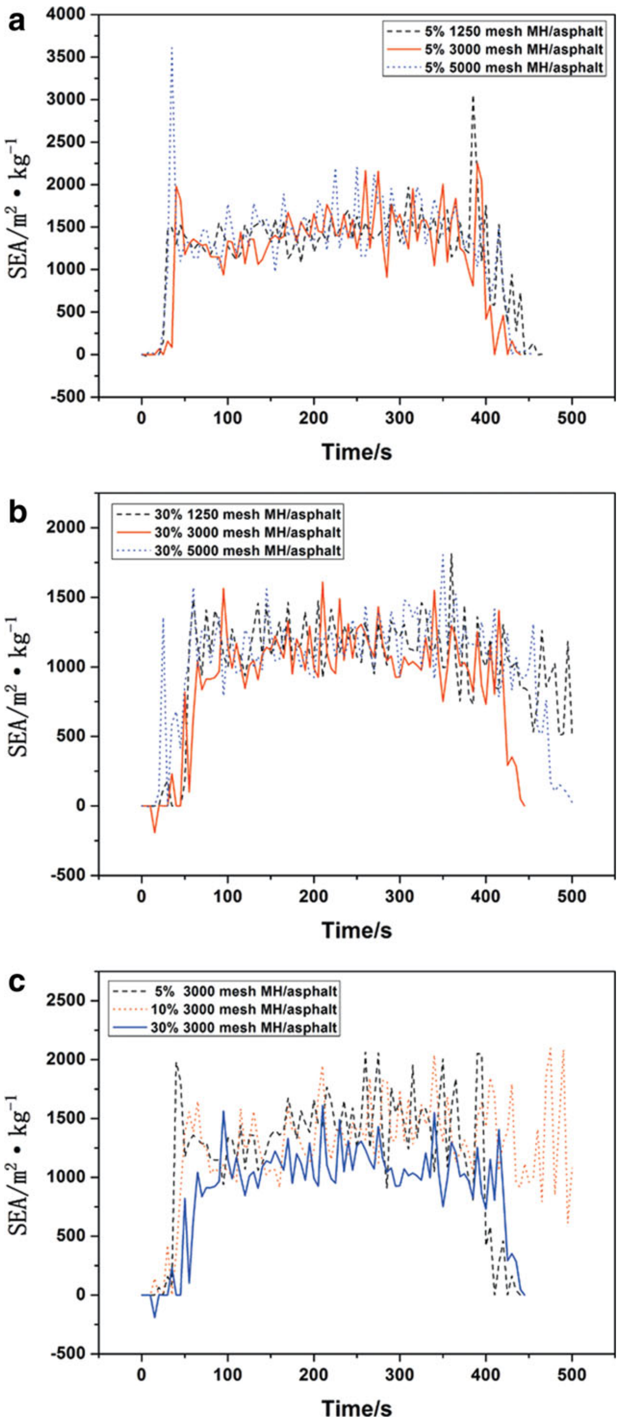

Figure 9. SEA curves of CONE test: (a) SEA curves for MH-filled asphalt at a MH content of 5% and different MH particle sizes; (b) SEA curves for MH-filled asphalt at a MH content of 30% and different MH particle sizes; (c) SEA curves for asphalt filled with different amounts of 3000 mesh MH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

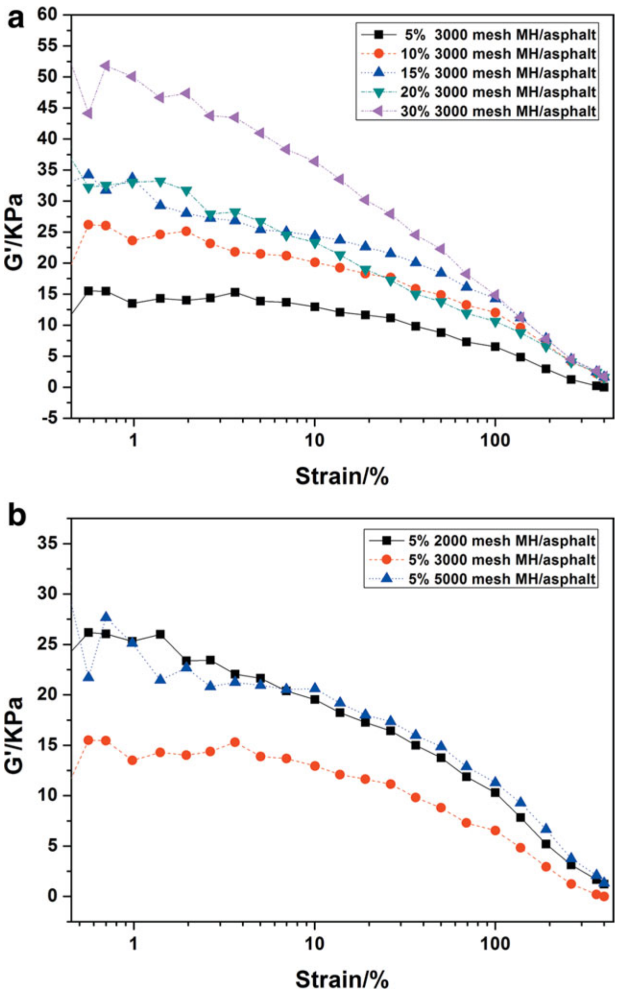

Figure 10. RPA curves of MH-filled flame-retardant asphalt samples: (a) RPA curves for 3000 mesh MH/asphalt composites at different MH contents; (b) RPA curves for MH/asphalt composites at a constant MH content of 5% and different MH particles sizes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The SEA is a measure of the smoke generation capacity of a burning material. The lower the SEA, the lower the smoke generation capacity and the stronger the effect of smoke suppression. Figure 9 shows the SEA curves of various MH-filled flame-retardant asphalt samples. A comparison of Figure 9(a,b) shows that at a MH content of 5%, 3000 mesh MH reduces the SEA more than other mesh MH. However, at high MH contents, the effect of MH particle size on the SEA is small. From Figure 9(c), we can observe that the SEA value of flame-retardant asphalt filled with 3000 mesh MH decreases with increasing MH content. Thus, the MH content is the major factor affecting SEA. In other words, increasing the content of MH can improve the smoke suppression effect, but the particle size of MH has no obvious effect on the smoke suppression.

Dispersion of MH in Asphalt

RPA. Figure 10 shows the RPA test results of MH-filled flame-retardant asphalt. From Figure 10(a) we can see that the modulus (G') response curve for asphalt filled with 5% of 3000 mesh MH is very flat, an indication that at this content the dispersion of MH in asphalt is uniform. With increasing content of MH, the modulus (G') response curve becomes steep; an indication that the dispersion of MH is getting worse and the MH forms the network gradually. The increase in shear modulus of the asphalt is due to the presence of the dispersed structure of the network. As the strain increases, the network-like structure is gradually destroyed, leading to a rapid decay of the modulus. We used low contents of MH to minimize operator error in the preparation of MH-filled flame-retardant asphalt. Figure 10(b) shows the RPA results of various MH/asphalt composites at a constant MH content of 5%, but different MH particle sizes. Because of the large particles and rod-like structure of the filler, flame-retardant asphalt filled with 2000 mesh MH has a high modulus. The modulus of 5000 mesh MH/asphalt is about the same as that of 2000 mesh MH/asphalt because of the agglomeration of 5000 mesh MH.

Environmental Scanning Electron Microscopy. An environmental scanning electron microscopy was used to observe the dispersion of MH in asphalt. 1250 mesh MH/asphalt, 3000 mesh MH/asphalt, 5000 mesh MH/asphalt, all at a MH content of 30%, were selected for observations.

It can be seen from Figure 11 that the 1250 mesh MH particles are uniformly distributed in the asphalt. Figure 12 shows that 3000 mesh MH particles are also uniformly distributed in the asphalt, with only a very small amount of MH agglomeration. Figure 13 shows varying degrees of agglomeration of the 5000 mesh MH particles in asphalt. With the decrease of MH particle size, the dispersion of MH in the viscous asphalt will become increasingly poor because superfine MH is prone to agglomeration. MH, as typical inorganic particles with a high surface energy, has a poor compatibility with the asphalt matrix, the saturated parts and aromatic parts of which consists of typical small organic molecules. Only the large particles of the MH can disperse well, while the small particles are easy to agglomerate and difficult to disperse because of the large surface area.

Effect of MH on Other Properties of Asphalt

Effect of MH on Viscosity of Asphalt. Figure 14 shows that with increasing MH content, the viscosity of MH/asphalt

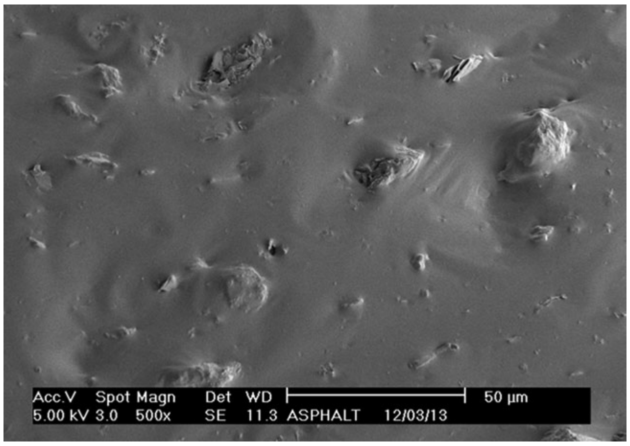

Figure 11. ESEM image of asphalt filled with 30% of 1250 mesh MH.

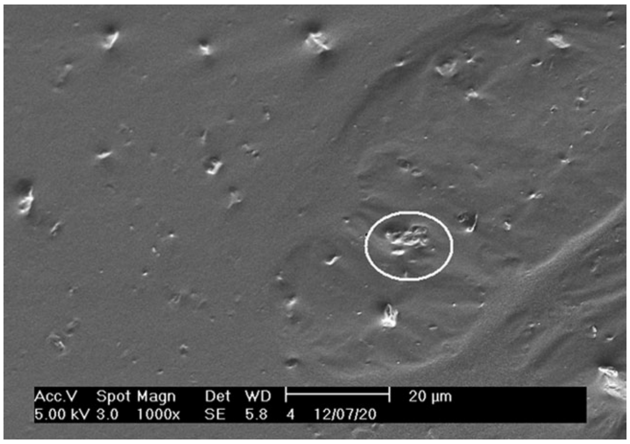

Figure 12. ESEM image of asphalt filled with 30% of 3000 mesh MH.

increases. When the MH content reaches 30%, all MH/asphalt composites, regardless of MH particle size, have a viscosity higher than 1 Pa.s, but are lower than the practical requirement of road construction of lower than 3 Pa.s. Such a viscosity does not affect the use of the asphalt in asphalt concrete. The viscosity generally increases with decreasing MH particle size at a given MH content. At MH contents below 20%, the viscosity at 2500 mesh is about the same as that at 5000 mesh and appears a big transition, probably because of the network-like structure of the MH.[18] The relationship between viscosity and volume fraction can express the formation of the network structure of dispersed MH better than the weight fraction. It can be observed that when the MH volume fraction increases to10%, the network structure formed by the dispersed MH makes the viscosity increase quickly in a so-called percolation phenomenon.

Effect of MH on Physical Properties of Asphalt. We selected asphalt filled with 3000 mesh MH to study the effect of MH content on the physical properties of MH/asphalt composite. Table VII show the test results of softening point, ductility, and penetration of various asphalt samples. MH can improve the high temperature resistance to deformation and the high temperature stability of the asphalt. At the same time, MH induces defects caused by stress concentration and destruction of the binding force between the asphalt molecules. As a result, MH reduces the ability of asphalt to resist low-temperature plastic deformation. Ductility slightly increases at a MH content of 5% than the pure asphalt because of the energy dissipation caused by interfacial slip and debonding. With further increases in MH

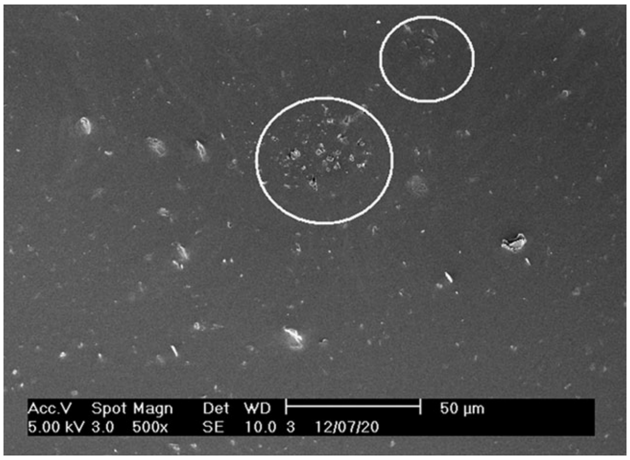

Figure 13. ESEM image of asphalt filled with 30% of 5000 mesh MH.

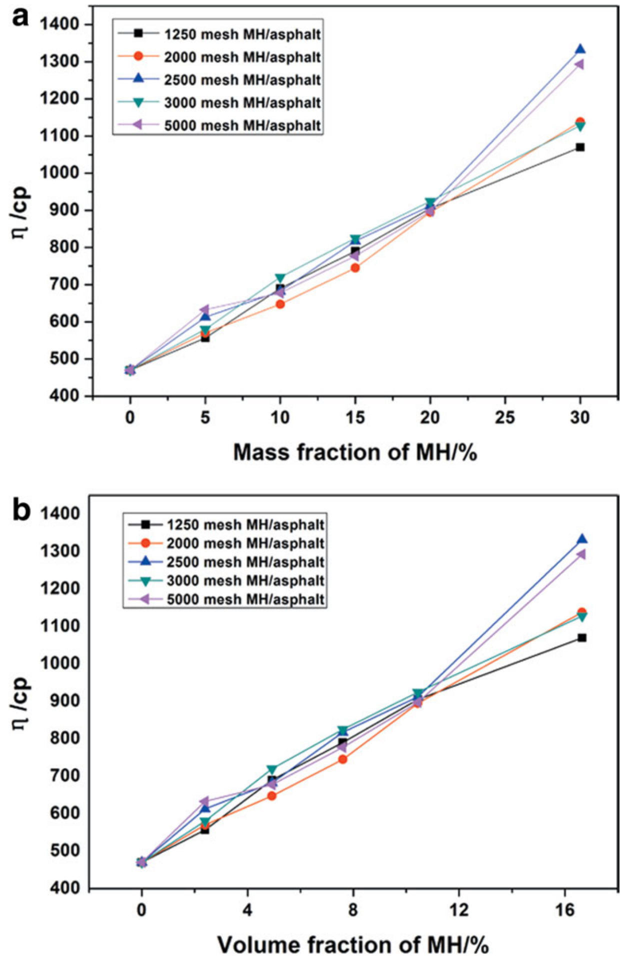

Figure 14. Viscosity curves of MH-filled flame-retardant asphalt: (a) Viscosity curves for MH/asphalt composites at different mass fraction; (b) Viscosity curves for MH/asphalt composites at different volume fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Physical Properties of 3000 Mesh MH/asphalt Composites at Different MH Contents

Samples	Softening point/°C	Ductility (5°C)/cm	Penetration (25°C)/dmm
Pure asphalt	46.0	9.2	79
5% 3000 mesh MH/asphalt	49.4	9.7	75
15% 3000 mesh MH/asphalt	51.9	7.2	68
30% 3000 mesh MH/asphalt	55.4	4.6	64

Table VIII. Asphalt and Gravel Adhesion Grade Standards

Stripping situation of asphalt membrane on the gravel surface after the test	Adhesion grade
Asphalt membrane fully saved, stripping percentage of the area close to 0	5
A small part of the asphalt membrane moved, uneven thickness, stripping percentage of the area less than 10%	4
Local asphalt membrane moved significantly but basically remain on the gravel surface, stripping percentage of the area less than 30%	3
Most of asphalt membrane moved but locally retained on the gravel surface, stripping percentage of the area greater than 30%	2
Asphalt membrane fully moved; the gravel basically was bare; asphalt all floated on the water	1

content, the cracks formed by interfacial debonding will quickly converge, resulting in early fracture.

Effect of MH on Gravel Adhesion of Asphalt. In accordance with the adhesion grading standards given in Table VIII, all the test samples shown in Figure 15, including pure asphalt and 3000 mesh MH/asphalt composites at MH contents of 5, 15, and 30% should all be rated grade 3. The same rating for pure asphalt and the MH/asphalt composites means that the addition of MH does not affect the adhesion between the asphalt and gravel.

CONCLUSIONS

1. Horizontal and vertical combustion method (UL94) showed that MH can significantly improve the flame-retardant properties of asphalt, but the particle size of MH did not show much influence on the flame-retardant properties. LOI tests showed that the LOI value increases with increasing MH content and mesh number. The LOI value did not further increase when the MH mass fraction reaches a certain level owing to the agglomeration of the superfine MH. We found that 3000 mesh is the optimum size of MH for flame-retardant asphalt.
2. The CONE tests showed the flame resistance performance of MH-filled asphalt in terms of endothermic dehydration, dilution of combustible gas, and isolation from oxygen. Increases in MH content and mesh are advantageous for decreasing the value of HRR and EHC. The best flame-retardant effect was obtained with 3000 mesh MH. The effect of MH particle size on smoke suppression was small.
3. RPA and ESEM analyses indicated that superfine MH particles easily aggregate in the sticky asphalt and affect the flame-retardant effect of the asphalt.
4. The particle size and content of MH had an effect on the viscosity of the asphalt. The results showed that even at a

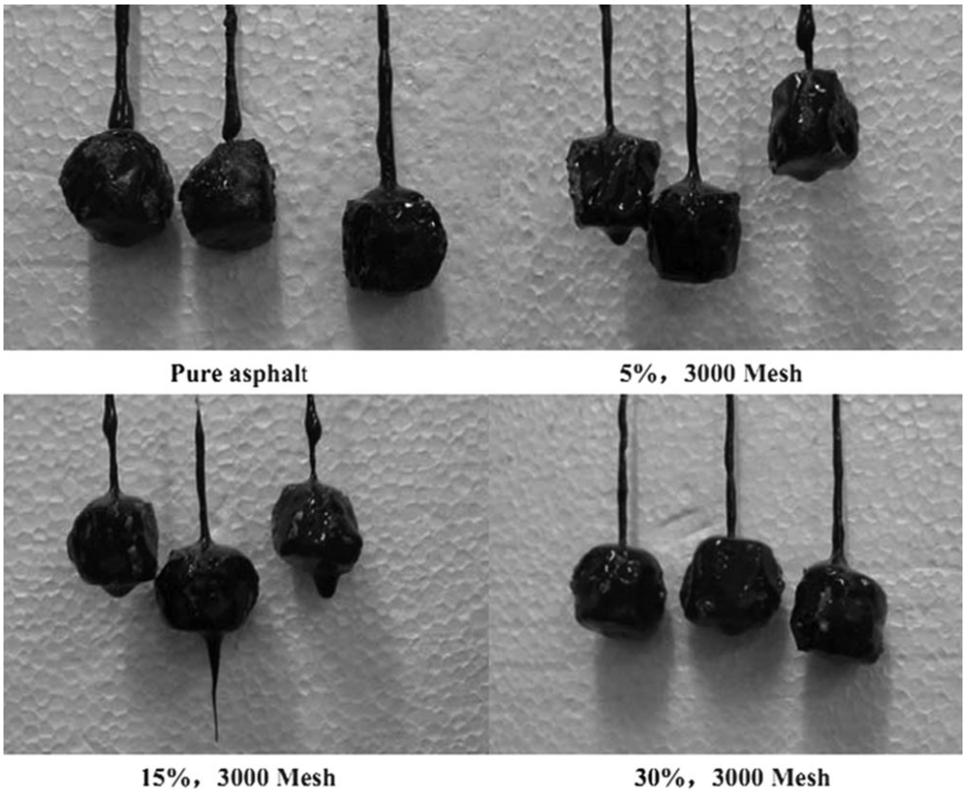

Figure 15. Adhesion test images of MH-filled flame-retardant asphalt samples.

MH content as high as 30%, the viscosity of MH-filled flame-retardant asphalt did not exceed 3 Pa.s regardless of the particle size of MH and did not affect the mixing and preparation of the asphalt.

5. The particle size and content of MH had an effect on the softening point, ductility and penetration of asphalt. As the MH content increased, the softening point of asphalt increased, but the ductility and penetration of asphalt decreased. MH improved the thermal stability of asphalt.
6. The particle size and content of MH had little effect on the adhesion between asphalt and gravel, even at an MH content as high as 30%.

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