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Effect of M-resin-based Stabilizer on the Performance of SBS Modified Asphalt

Zhen LEI [1], Zhirong JIA [2]*, Xuefeng LIN [1], Chaoyu LI [1], Heng LIU [1], Jing ZHANG [2]

[1] *School of Transportation and Vehicle Engineering, Shandong University of Technology, Zibo 255049, China*
[2] *School of Civil and Architecture Engineering, Shandong University of Technology, Zibo 255049, China*

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Industrial solid waste M-resin (MR) contains high sulfur content which was difficult to be comprehensively utilized. According to the vulcanization reaction mechanism, MR was used as vulcanizing agent, nano zinc oxide (ZnO) as an activator, tetramethyl thiuram disulfide (TMTD) as an accelerator to produce M-resin-based stabilizer. MR (0.5, 1, 1.5, 2, 2.5), ZnO (0.1, 0.2, 0.3, 0.4, 0.5) and TMTD (0.06, 0.08, 0.1, 0.12, 0.14) were mixed with different contents, a three-factor and five-level orthogonal experiment was designed to test the penetration, ductility, softening point and 48 h softening point difference of SBS modified asphalt. Based on the four indexes, the basic formula of the stabilizer was obtained. The influence of kaolin, an auxiliary material, on the thermal stability was compared, and the formula were optimized, the appropriate dosage was determined. The microscopic morphology of the modified asphalt and SBS developmental fineness was analyzed with the fluorescent microscopy technology, and the SBS developmental fineness was studied with the generated binary graph and skeleton graph. DSR test was carried out to detect rheological properties of modified asphalt with different dosages of MR-based stabilizes. The results show that MR can significantly improve the thermal storage stability of modified asphalt. The ratio of MR:TMTD:ZnO:Kaolin is 1.5:0.5:0.08:12, and the appropriate dosage is 1.02 %. The stabilizer can reduce the 48 h softening point difference 33.6 ℃, increase the softening point 13.6 ℃, decrease the penetration degree 9.7 mm, but it has little effect on 5 ℃ ductility index. The microscopic images show that a cavity two-phase continuous network structure is formed inside the modified asphalt under the appropriate dosage of M-resin-based stabilizer. The SBS developmental fineness is 2.36 μm, and the uniformity is good. DSR test also shows that stabilizer can effectively improve the high temperature performance of SBS modified asphalt.
Keywords: M-resin, modified asphalt, stabilizer, thermal storage stability, developmental fineness.

1. INTRODUCTION

M-resin (MR) is a by-product of the high-pressure reaction process that produces promoter M in the industry. In 2020, the annual output of promoter M is about 200,000 to 300,000 tons in China, and the amount of MR is about 20,000 to 30,000 tons. According to the "National Directory of Hazardous Wastes" (2016 Edition), MR belongs to HW13 organic resin waste. MR is yellow and viscous at room temperature, low density, has no fluidity but foul smell. If not reasonably disposed, MR is difficult to be degraded in nature, and it will pile up and occupy land, and pollute the environment [1]. Treatment methods for MR mainly include thermal cracking, incineration, landfill, etc. When MR is burned as fuel, not only does the way generate harmful gases such as sulfur dioxide, nitrogen dioxide, and hydrogen sulfide which cause air pollution, but also causes the waste of sulfur in MR [2–5]. The elemental sulfur content is 18.79 %, the elemental sulfur and the combined sulfur total about 38 % in MR which is easy to be melted at high temperature. If MR were actively used in asphalt pavement based on the environmental protection concept and the needs of road construction engineering that would realize the win-win results of cost reduction and environmental protection.

MR is modified and added to a modified asphalt stabilizer as a vulcanization reaction promoter to promote the vulcanization cross-linking reaction between sulfur and modified asphalt [6]. It is also added to the concrete as additives, and used to improve the toughness of the curing agent, and mixed into asphalt to make low-grade water proofing asphalt membranes, but the improvement effort is not ideal [7]. Experiment shows that 2-mercaptobenzothiazolein MR has a certain cross-linking effect when incorporated into polymer modified asphalt as a substitute for sulfur [8]. The possibility is also discussed that MR used as a dulterating agent to make composite modified asphalt in pavement engineering [9].

Sulfur, tetramethyl thiuram disulfide, zinc oxide, butylated hydroxytoluene, kaolin, and carbon-white can be used as raw materials of modified asphalt stabilizer [10, 11]. High temperature rheological properties of SBS modified asphalt can be evaluated by dynamic shear rheometer, and temperature sweep tests provide more reliable results for detecting the rheological properties of modified asphalt [12]. The improvement of the high temperature storage stability of modified asphalt can be attributed to the reduction of density difference between SBS and asphalt by kaolin [13]. After the incorporation of nano-ZnO, the segregation softening point difference of SBS modified asphalt after 48 h is significantly reduced [14]. TMTD can effectively improve the thermal storage stability and anti-aging performance of SBS modified asphalt [15].

Stabilizing effect of the stabilizer is evaluated by softening point difference between the upper and lower sections of bituminous aluminum tube samples stored at

*Corresponding author. Tel.: +86-151-6922-7677.
E-mail address: *jiazhr@126.com* (Z. Jia)

163 °C for 48 h [16, 17]. Different stabilizers have different effects on different indexes of modified asphalt, and the improvement of performance indexes of modified asphalt is also different. Good stabilizers can be prepared by adding different auxiliary components [18 – 20]. Fluorescence microscopy is widely used in the field of polymer modified asphalt [21]. This technology can evaluate the quality and performance of modified asphalt, and observe the real phase structure of SBS in the asphalt system, analyze the micro-morphology of SBS, auxiliary evaluate the stability effect of stabilizer [22 – 26].

There are few researchers on the application of MR as stabilizer in the field of road engineering at home and abroad. According to the physical performance indicators of the modified asphalt, this paper expects to obtain the stabilizer formula for using MR as the vulcanizing agent, determine the appropriate dosage, and evaluate the stable effect of the MR stabilizer by microscopic analysis, and provide technical support of MR application in asphalt pavement.

2. RAW MATERIAL

2.1. Matrix asphalt

Use 70# A grade Qilu asphalt as raw material. Performance indexes are shown in Table 1.

Table 1. 70# A grade Qilu asphalt

Index	Result
25 °C penetration, 0.1 mm	69
Softening point, °C	48.6
10 °C ductility, cm	40
15 °C ductility, cm	> 150
Density, g/cm^3	1.033
60 °C dynamic viscosity, Pa•S	218
Flash point, °C	296

2.2. M-resin

M-resin is provided by Shangshun Chemical Company. The blocky M-resin (Fig. 1 a) was crushed, ground and passed through a 50 mesh sieve (Fig. 1 b).

a b

Fig. 1. M-resin sample

2.3. Vulcanization accelerator

The vulcanization accelerator (TMTD) was produced by Shanghai Dibo Chemical Company. It can activate M-resin, increase curing rate, decrease curing temperature and accelerate vulcanization cross-linking reaction. Material indexes are shown in Table 2.

Table 2. TMTD

Index	Result
Appearance	White powder
Melting point, °C	> 142
Heating loss, %	> 0.3
Ash, %	> 0.3
150 μm material retained, %	> 0.1
Fineness, mesh	200

2.4. Active agent

Nanometer-zinc oxide can promote cross-linking reaction between modifiers. Material indexes are shown in Table 3.

Table 3. ZnO

Index	Result
Molecular weight	81.39
AR, %	> 99.0
Density, g/cm^3	5.608
Sulfur compounds, %	< 0.01
Mean diameter, nm	50

2.5. Auxiliary ingredient

Kaolin can reduce the difference between SBS particle density and asphalt density and improve rheological properties of modified asphalt. Material indexes are shown in Table 4.

Table 4. Kaolin

Index	Result
Al_2O_3, %	44.28
SiO_2, %	52.32
Fe_2O_3, %	0.43
PH	7.2
Density, g/cm^3	2.56
Ignition loss, %	9

2.6. Preparation of SBS modified asphalt

The modified asphalt samples were prepared by the same preparation process, and the process method is shown in Fig. 2. The MR stabilizer is dry powder and can be directly add into modified asphalt.

3. EXPERIMENT

The mass fraction of MR in stabilizer formula was the mass of sulfur in MR. In the orthogonal test, the dosage of MR stabilizer in 25 working conditions was 0.1 %.

3.1. Basic formulation orthogonal experimental design

MR (0.5, 1, 1.5, 2, 2.5), nano ZnO (0.1, 0.2, 0.3, 0.4, 0.5) and TMTD (0.06, 0.08, 0.1, 0.12, 0.14) were used as raw material. A three-factor and five-level orthogonal experiment which contains twenty-five working conditions was carried out. The basic formula of stabilizer was selected according to penetration, ductility, softening point and 48h softening point difference in 25 working conditions.

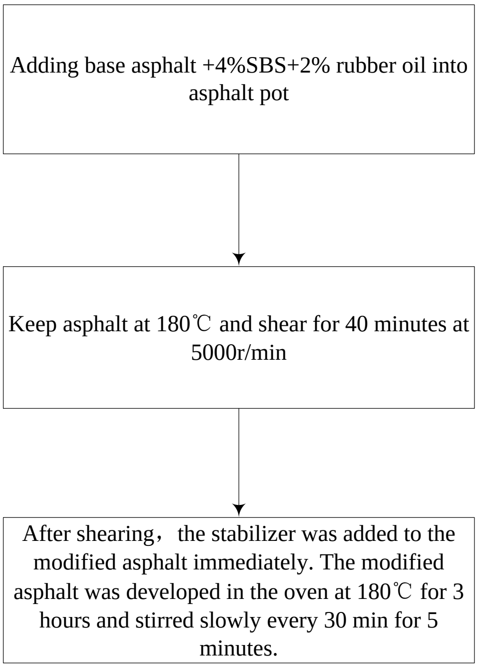


Fig. 2. Fabrication flow chart

3.2. Formula optimization experiment

The stabilizer dosage of the basic formula was maintained at 0.1 %. A comparative test was carried out by admixing auxiliary ingredient kaolin. The quality of MR was got based on the basic formula and dosage, and kaolin was calculated according to MR: Kaolin = 1:2, 1:4, 1:6, 1:8, 1:10. After modified asphalt samples were prepared, a 48 h segregation softening point difference was tested. The stabilizer formula was determined by a minimum 48 h softening point difference index.

3.3. Conventional index experiment of modified asphalt with stabilizer

Based on the stabilizer formula, the modified asphalt samples were prepared with stabilizer dosages of 0 %, 0.34 %, 0.68 %, 1.02 %, and 1.35 %. The penetration, ductility, softening point, and 48h softening point difference of modified asphalt were carried out respectively according to the *Highway Engineering Asphalt and Asphalt Mixture Test Regulations* (JTG E20-2011). The test data were recorded and the influence law was analyzed, the appropriate dosage was determined eventually.

3.4. Fluorescent microscopy analysis

Due to the large difference in density between SBS modifier and matrix asphalt, SBS particles in asphalt will float up when stored at high temperatures. It is essential to observe the bottom third section of modified asphalt samples from a micro perspective. After being stored at 163 °C for 48 hours, the bottom third modified asphalt with stabilizer dosage of 0 %, 0.34 %, 0.68 %, and 1.02 %was selected to prepare microscopic samples by using slides and cover glasses. The samples were observed and photographed under a fluorescent microscope at 40 times, 100 times, and 400 times, and microscopic images were compared and analyzed under the different dosages of stabilizer.

3.5. Quantitative analysis of developmental fineness

MATLAB was used to obtain the binary map and skeleton map of the bottom third modified asphalt with different dosages of stabilizer at 400 times and carried out a quantitative analysis of developmental fineness.

3.6. Rheological properties

DSR test was carried out to record the rutting factor of modified asphalt samples under medium and high temperature environments.

4. DATA ANALYSIS

4.1. Basic formulation orthogonal experimental design

The L25 orthogonal table was used to carry out the orthogonal experiment of the formula of M-resin-based stabilizer. Test results are shown in Table 5.

With the increase of the MR mass fraction in the stabilizer, the softening point gradually increases, and the 48h softening point difference gradually decreases, but the penetration index shows a decreasing trend, and the effect on the 5 ℃ ductility is not significant. This shows that excessive MR would reduce the penetration, and reduce the 5 ℃ ductility index of the modified asphalt which became gelled.

The best softening point index for test No. 23 is 76.2 ℃, and the ratio of each factor of the formula is MR:TMTD:ZnO = 2.5:0.3:0.08; the 48h segregation softening point difference of test No.24 is the smallest, 12.4℃, and the ratio of each factor of the formula is MR:TMTD:ZnO = 2.5:0.4:0.1. The softening point index of test No.15 is only 0.8℃, lower than that of No.23, and the softening point difference index of 48h is only 0.6℃ higher than that of No. 24, but it is better than both in penetration and 5 ℃ ductility. The mixing ratio of M-resin-based stabilizer formula is MR:TMTD:ZnO = 1.5:0.5:0.08 in orthogonal experiment.

The influence of different factors on the softening point index is shown in Table 6. The order of influence of various factors on the softening point index can be seen by the size of R value, the order is MR > TMTD > ZnO, the most important factor affecting the softening point index is MR, followed by TMTD, and finally ZnO. Use the same method to calculate the influence of each factor on penetration, ductility, and 48 h segregation softening index. The influence law of each factor is the same as the softening point according to the R value.

4.2. Formula optimization experiment

When the ratio of M-resin-based stabilizer is MR:TMTD:ZnO = 1.5:0.5:0.08 according to the orthogonal experiment, the 48h softening point does not meet the requirement of ≤ 2.5 ℃ gave by Highway Engineering Asphalt and Asphalt Mixture Test Regulations (JTG E20-2011). Therefore, a comparative test of Kaolin was carried out based on the basic formulation. The test results are shown in Table 7.

Table 5. Orthogonal test results of M-resin-based stabilizer formulation

Test number	Factor			Softening point, ℃	Penetration 25 ℃, 0.1 mm	5 ℃ ductility, cm	48 h softening point difference, ℃
	MR	TMTD	ZnO				
1	0.5	0.1	0.06	70.1	63.86	26.5	27.9
2	0.5	0.2	0.08	70.8	63.22	26.7	26.3
3	0.5	0.3	0.1	70.9	62.85	26.8	25.8
4	0.5	0.4	0.12	71.3	62.54	27.1	25.4
5	0.5	0.5	0.14	71.6	62.24	26.9	24.8
6	1	0.1	0.08	72.1	59.97	27.6	23.1
7	1	0.2	0.1	73.3	58.67	27.4	22.8
8	1	0.3	0.12	72.8	59.12	27.8	21.5
9	1	0.4	0.14	73.5	58.39	27.1	21.1
10	1	0.5	0.06	72.9	58.18	27.5	19.6
11	1.5	0.1	0.1	73.9	56.38	28.1	18.4
12	1.5	0.2	0.12	74.3	56.52	27.8	16.7
13	1.5	0.3	0.14	74.1	55.83	28.2	15.3
14	1.5	0.4	0.06	74.4	55.57	28.6	14.6
15	1.5	0.5	0.08	75.4	55.32	28.2	13.1
16	2.0	0.1	0.12	74.6	55.23	27.7	14.2
17	2.0	0.2	0.14	75.1	54.61	27.0	13.8
18	2.0	0.3	0.06	74.7	54.96	27.4	12.7
19	2.0	0.4	0.08	75.8	54.41	27.3	13.2
20	2.0	0.5	0.1	75.1	53.97	27.1	12.9
21	2.5	0.1	0.14	75.3	53.83	27.5	13.3
22	2.5	0.2	0.06	75.1	53.42	26.8	12.9
23	2.5	0.3	0.08	76.2	53.37	25.8	13.1
24	2.5	0.4	0.1	75.6	53.10	26.2	12.4
25	2.5	0.5	0.12	75.8	53.02	25.6	12.5

Table 6. Analysis of the influence of softening point index

Visual analysis	Factor		
	MR	TMTD	ZnO
Average value K1	70.94	73.2	73.44
Average value K2	72.92	73.62	74.06
Average value K3	74.42	73.74	73.76
Average value K4	75.06	74.12	73.76
Average value K5	75.6	74.16	73.92
Range	4.66	0.96	0.62

Table 7. Kaolin optimization experiment

MR: Kaolin	Segregation -48 h softening point difference, ℃					Remarks
Kaolin blending ratio	1	2	3	4	average value	
1:2	10.2	9.1	9.3	9.4	9.5	Not gelled
1:4	8.1	7.8	7.3	7.9	7.8	Not gelled
1:6	5.2	5.1	4.2	4.3	4.7	Not gelled
1:8	2.5	2.2	2.3	2.2	2.3	Not gelled
1:10	2.8	2.1	2.5	2.6	2.5	Slightly gelled

Table 8. The dosage experimentof M-resin stabilizer formulation

Stabilizer dosage/%	Softening point, ℃	Penetration 25℃, 0.1 mm	5℃ ductility, cm	48 h softening point difference, ℃	Remarks
0	65.6	64.62	26.2	34.8	Not gelled
0.34	70.8	58.47	27.3	11.6	Not gelled
0.68	75.9	56.43	27.9	2.3	Not gelled
1.02	78.7	55.12	28.2	1.1	Not gelled
1.35	–	–	–	–	Gelled

Analyzing the data in Table 7, it is known that when the kaolin content (relative to MR) is 800 %, the 48 h segregation softening point difference of the modified asphalt can reach the minimum 2.3 ℃, which meets the requirement of ≤ 2.5 ℃. When the dosage of kaolin continues to increase, the 48 h segregation softening point difference no longer decreases, and there is an upward trend. The formula of M-resin-based stabilizer is adjusted to MR:TMTD:ZnO:Kaolin = 1.5:0.5:0.08:12.

According to the data in Table 8, when the dosage of M-resin-based stabilizer is 1.35 %, the pole climbing phenomenon will appear on the high-speed shearing machine. The modified asphalt will be slightly gelled. According to the performance of modified asphalt, the appropriate dosage of M-resin-based stabilizer is determined to be 1.02%. The influence on the performance of modified asphalt is shown in Fig. 3, Fig. 4, Fig. 5, Fig. 6.

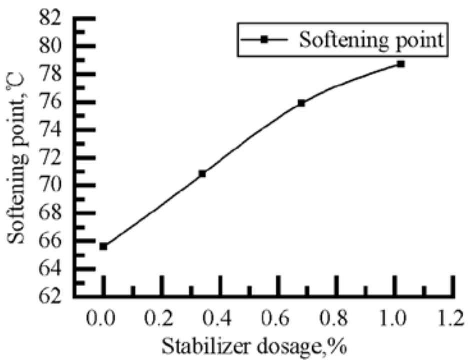


Fig. 3. Softening point versus stabilizer dosage

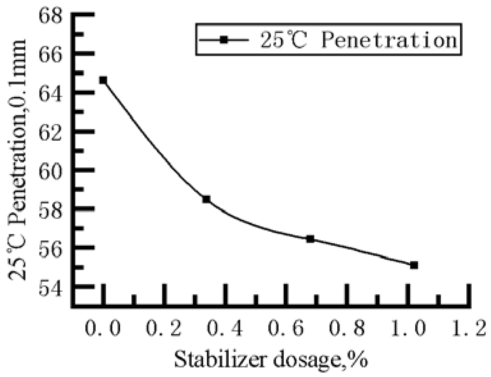


Fig. 4. Penetration versus stabilizer dosage

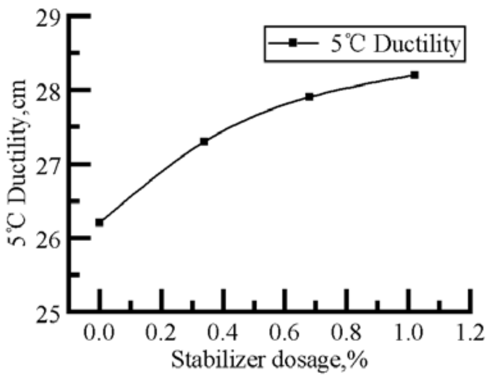


Fig. 5. Ductility versus stabilizer dosage

It can be got from Fig. 1, Fig. 2, Fig. 3 and Fig. 4, with the increase of stabilizer dosage from 0 % to 0.34 %, the softening point increases by 5.2 ℃, the penetration at 25 ℃ decreases by 0.615 mm, and the 5 ℃ ductility increases by 1.1 cm.

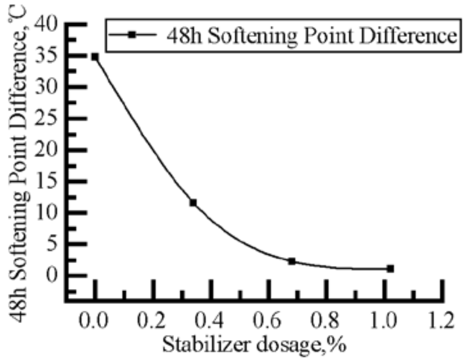


Fig. 6. 48 h softening point difference versus stabilizer dosage

With the increase of stabilizer dosage from 0.34 % to 0.68 %, the softening point increases by 5.1 ℃, the penetration at 25 ℃ decreases by 0.204 mm, the 5 ℃ductility increases by 0.6 cm. With the increase of stabilizer dosage from 0.68 % to 1.02 %, the softening point increases by 2.8 ℃, 25 ℃ penetration decreases by 0.131 mm, and 5 ℃ ductility increases by 0.3 cm. With the increase of the M-resin-based stabilizer dosage, the softening point and viscosity increased gradually. The 48 h softening point difference is reduced significantly, showing good thermal storage stability, and the effect on the 5 ℃ ductility was not significant, only slightly increases. Excessive M-resin-based stabilizer will cause excessive internal cross-linking of the modified asphalt, causing gelation of the modified asphalt, which is not conducive to pumping of the modified asphalt.

4.4. Fluorescent technology analysis

A fluorescent microscope was utilized to observe and photograph microscopic samples at 40, 100, 400 times. Various multiples fluorescent micrographs are shown in Fig. 7, Fig. 8, Fig. 9, Fig. 10.

Comparing the microscopic pictures of modified asphalt with different dosages of stabilizer under the same multiples in Fig. 7, Fig. 8, Fig. 9, Fig. 10, it is found that the microscopic samples of the bottom third modified asphalt with different dosages of the M-resin-based stabilizer have obvious differences in fluorescent photography. When the dosage is 1.02 %, the yellow fluorescent image is clearer, the SBS modifier number is increased which is observed under the same multiple, the SBS swells well, and the distribution uniformity is better. It can be observed from the fluorescent photo at 400 times that the swollen SBS fine particles begin to connect, and there is no aggregation to form large SBS particles, which is beneficial to the improvement of the thermal storage stability of the modified asphalt.

4.5. Detailed quantification analysis

Binary images and skeleton images are obtained by using MATLAB program to process the microscopic pictures of modified asphalt samples at 400 times, and the area ratio and developmental fineness of SBS are calculated respectively to evaluate the stabilizing effect of M-resin-based stabilizer. After reading the total number X of white pixels in the binary image, the program performs skeletonization. The skeleton line is the center line of the white part in the binary image. The program read the number of white pixels in the center line of the skeleton, which is the length Y of the center line. Use Autocad software to divide the binary image into 8 μm × 8 μm small squares, read the number of pixels in the side length direction, and read the number of side length pixels as 33, thereby, the actual length of one pixel is 8/33 (μm/pix), and the developmental fineness is calculated [25]. The test results are shown in Table 9.

It can be seen from fluorescent photography at 400 times in Table 9, with the increase of the stabilizer dosage, the network structure becomes increasingly obvious, the distribution of SBS is more uniform, and the developmental fineness is also improved. When the developmental fineness is 1.56 μm, SBS is dispersed in the asphalt forming a single-phase continuous structure. when the developmental fineness is between 2.25 – 2.36 μm, SBS and asphalt intersect each other, and the area ratio of the two phases is close to 1:1. A two-phase continuous network structure with cavities makes the two tightly combined, and the SBS performance is transferred to the asphalt to obtain a better modification effect. Studies have shown that a two-phase continuous network structure is the most ideal decentralized state. When the developmental fineness of SBS particles is less than 2 μm, SBS is single phase continuous in the asphalt. When the developmental fineness of SBS particles is between 2.3 μm and 2.6 μm, the modification effect is better [22].

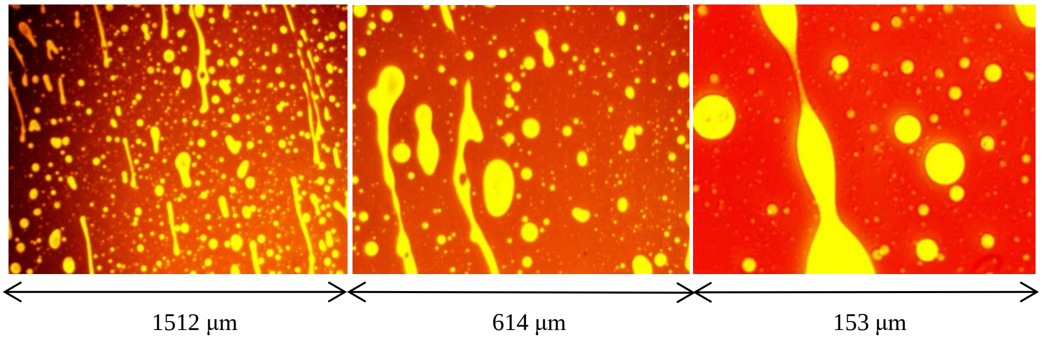


Fig. 7. Microscopic image of 0 % M-resin stabilizer

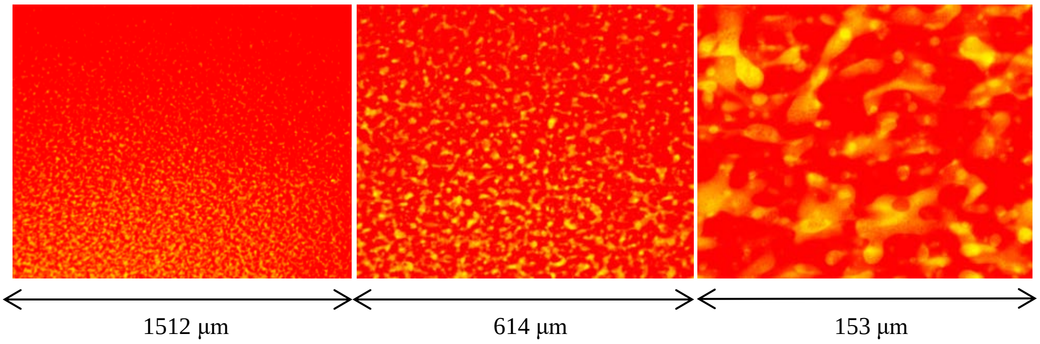


Fig. 8. Microscopic image of 0.34 % M-resin stabilizer

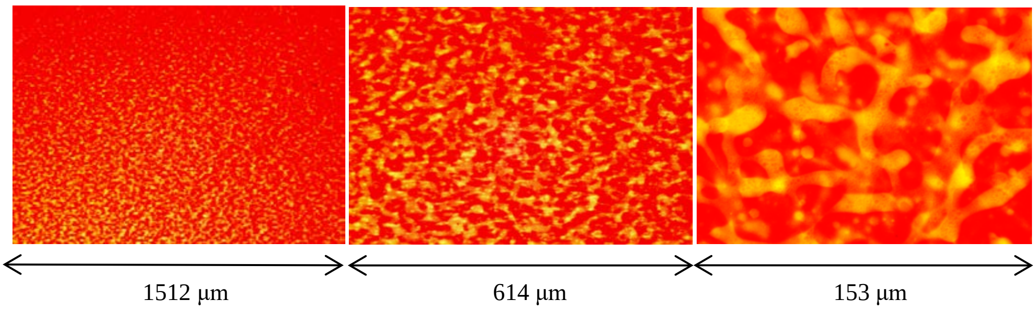


Fig. 9. Microscopic image of 0.68 % M-resin stabilizer

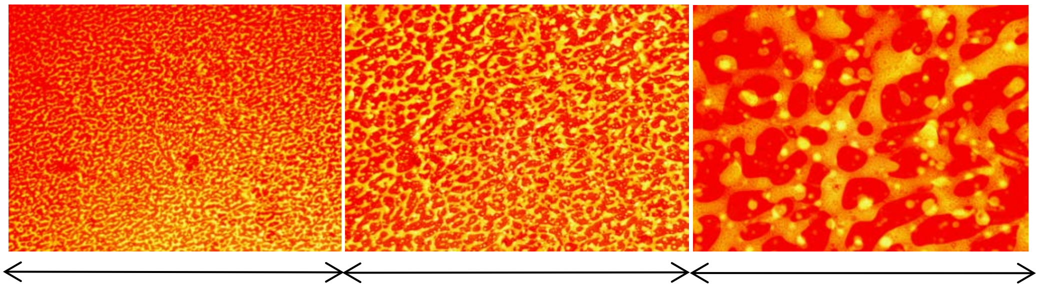
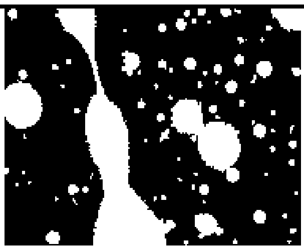
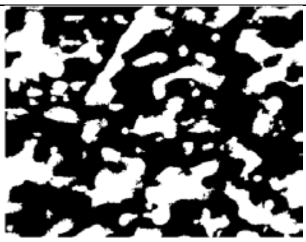
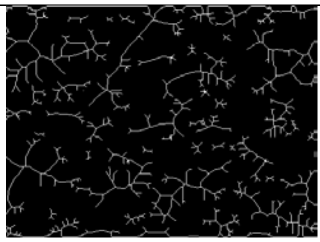
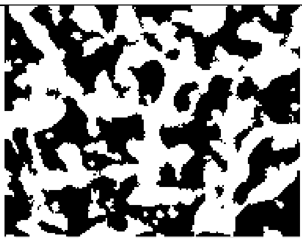
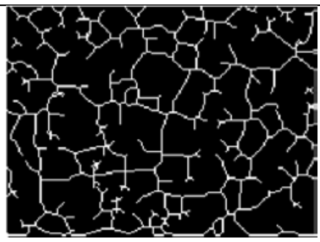
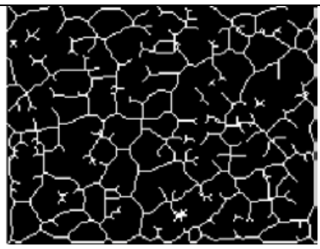


Fig. 10. Microscopic image of 1.02 % M-resin stabilizer

Table 9. 400 times microscopic quantitative results of M-resin-based stabilizers with different dosage

Stabilizer dosage	Binary graph 153 μm	Skeleton diagram 153 μm	SBS area ratio, %	Relative fineness of development (X/Y)	Actual development fineness, μm
0 %			24.05	6.42	1.56
0.34 %			35.48	8.83	2.14
0.68 %			42.30	9.26	2.25
1.02%			47.07	9.72	2.36

4.6. Rheological properties

The dynamic shear rheometer was produced by Malvin Company, shown in Fig. 11. The bottom third modified asphalt samples were prepared after being stored at 163 ℃ for 48 h. Temperature sweep tests were carried out with temperature scanning range 55 – 82℃. The rutting factor was obtained by the DSR test, and used to evaluate the high temperature performance of modified asphalt.

The results of the temperature sweep test were shown in Fig. 12. The rutting factor increased when the MR based stabilizer was added. When the added dosage from 0 % to 1.02 %, the 58 ℃ rutting factor increase from 6.91 kPa to 14.08 kPa, the 64 ℃ rutting factor increase from 3.82 kPa to 7.23 kPa.

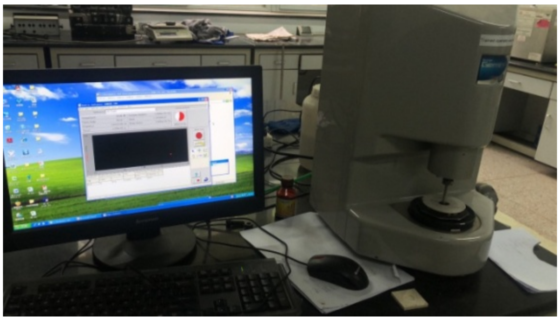


Fig. 11. Dynamic shear rheometer

The MR-based stabilizer can effectively improve the high temperature performance of SBS modified asphalt.

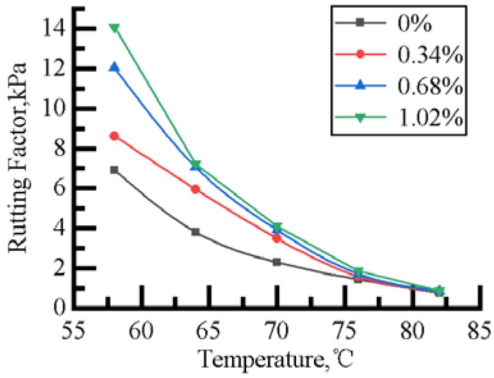


Fig. 12. Rutting factor

4.7. Cost analysis

By surveying, the unit price of industrial sulfur powder in China is about 9,000 RMB/t, TMTD accelerator is about 200,000 RMB/t, nano ZnO is about 80,000 RMB/t, and kaolin is about 3,600 RMB/t, the cost of processing M-resin is about 2,200 RMB/t. The prices of sulfur based stabilizer and MR based stabilizer are shown in Table 10. If M-resin replace sulfur as a vulcanizing agent, 2247 RMB/t can be saved.

Table 10. Price of the stabilizers

Stabilizer	Price, RMB/t
Sulfur based	11,501.2
MR based	9,253.6

5. CONCLUSIONS

1. The basic formula of M-resin-based stabilizer is MR:TMTD:ZnO:Kaolin = 1.5:0.5:0.08:12, and the appropriate dosage is 1.02 %. The content of MR in the stabilizer has the most significant impact on the performance indicators of modified asphalt. Excessive M-resin-based stabilizer will cause exorbitant cross-linking of modified asphalt and appear a gelated phenomenon.
2. The addition of M-resin-based stabilizer greatly improves the thermal storage stability of the modified asphalt, improves the softening point of the modified asphalt, reduces the penetration, and increases the viscosity. It has no obvious impact on the ductility index. The test results show that MR can be used as a cross-linking agent instead of sulfur.
3. The fluorescent micrograph reflects the influence of M-resin-based stabilizer on the dispersive effect of SBS modifier in asphalt. Under the appropriate dosage of M-resin-based stabilizer, the SBS modifier in the bottom third of modified asphalt increases after storing at 163 °C for 48 h, and the fluorescent part become more and more obvious. The area ratio of the two phases is close to 1:1, and the distribution uniformity is good.
4. It is found that the addition of stabilizers improved the developmental fineness of the SBS modifier in the modified asphalt by using the MATLAB program to quantitatively analyze the photographs of modified asphalt samples with different dosages of M-resin stabilizer at 400 times. Under 1.02 % dosage of M-resin-based stabilizer, the developmental fineness is 2.36 μm, the modification effect is good, and a two-phase continuous network structure with cavities is formed. In general, the macro performance of the modified asphalt mixed with stabilizers corresponds to the microanalysis results.
5. According to the results of fluorescence microscopy and rheological analysis, MR based stabilizer has positive effect on SBS modification.
6. The influence of other complex components of M-resin on modified asphalt should be studied next, and the reaction mechanism should be studied deeply by infrared spectroscopy, etc.

Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

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