Aging Mechanism of SBS Modified Asphalt Based on Chemical

Reaction Kinetics

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1 **Abstract:** Research on aging mechanism of SBS modified asphalt can provide
2 theoretical and technical support not only for the choice of asphalt pavement materials
3 but also for recycling of SBS modified asphalt pavement. Dynamic equations of
4 asphalt under different aging conditions were respectively established according to
5 chemical reaction kinetics. And two kinds of micro analysis methods, component
6 analysis and GPC (gel permeation chromatography), were used to analyze the change
7 of asphalt composition and asphalt molecular structure during the aging process. In
8 addition, the correlation between activation energy and asphalt microscopic
9 components, asphalt molecular structure was analyzed through grey entropy theory
10 analysis method. Different from previous research, the results demonstrate that the
11 activation energy of asphalt is not a constant index. SBS network structure loses
12 gradually due to the degradation of SBS modifier during the aging process. SBS
13 modified asphalt after short-term aging degrades to more medium molecular size
14 structure, which makes the activation energy become lower and improves asphalt
15 temperature sensitivity. However, the SBS modifier after long-term aging has almost
16 degraded completely, which increases the activation energy and makes asphalt
17 temperature sensitivity approximate to base asphalt. The results of grey entropy
18 theory analysis show that the activation energy will be reduced with the decrease of
19 saturate content, the increase of medium molecular size structure content and resins
20 content.

21 **Keywords:** SBS modified asphalt, chemical reaction kinetics, aging mechanism,
22 component analysis, Gel Permeation Chromatography

23

1. Introduction

Asphalt aging has been recognized as an important aspect in asphalt research. Asphalt binder aging occurs during the mixing and construction process as well as during service process in the road. Due to the oxidation, the aging process will result in the loss of volatile components and reorganization of asphalt binder molecules. The aging of asphalt binder is an oxidative chemical process that will lead to the formation of carbonyl compounds and sulfoxides. Then, the stiffness, adhesion and flexibility properties of binder will be affected [1]. Consequently, aging of asphalt binder has a direct impact on road performance. During the service process of asphalt pavement, the asphalt will become stiffer and more brittle due to oxidation, sunlight and ultraviolet radiation. However, the oxidation is the main factor. More importantly, asphalt peeling off from aggregate surface, pumping slurry, loose, threshing forming pit slot and water seeping into middle or lower layer can also cause water damage. All these will influence the performance and service function of asphalt pavement significantly [2-4]. Therefore, understanding the aging mechanism of asphalt can have a significant role in pavement maintenance, choosing the asphalt materials, strengthening durability of the pavement, and recycling SBS modified asphalt pavement that will save resources and reduce the pressure of environment.

Owing to the increasing traffic, ordinary asphalt pavement has been gradually unable to meet the needs of transportation and environment. Recently, researches and engineering practices have shown that SBS (styrene-butadiene-styrene block copolymers) modifier can comprehensively improve pavement performance[5].

1 Nowadays, a number of freeways have required rehabilitation or reconstruction in
2 China, which produces a lot of aged SBS modified asphalt mixture. The abandonment
3 of these materials not only wastes resources, but also causes environmental pollution
4 and excessive exploitation of new natural resources [6]. Therefore, recycling of the
5 aged SBS modified asphalt mixture has become increasingly priority in the highway
6 industry.

7 Though researchers have paid more attention to the aging mechanism of SBS
8 modified asphalt. However, studies mainly focused on evaluating and analyzing the
9 change of performance indicators before and after aging from the superficial
10 phenomenon. For instance, Airey et al. carried out a large amount of experimental
11 research for SBS modified asphalt after RTFOT and PAV aging and discussed the
12 differences of aging performance between SBS modified asphalt and base asphalt [7].
13 The results indicated that the aged asphalt containing more modifiers showed more
14 viscous characteristics rather than usually imagined elastic characteristics. And the
15 transformation to viscous flow state for SBS modified asphalt was mainly due to the
16 degradation of SBS modifiers.

17 Paling et al. evaluated the influence of different aging states on asphalt high
18 temperature performance, low temperature crack resistance and temperature
19 sensitivity through penetration, penetration index, ductility, softening point, etc. test
20 indexes. The results showed that the addition of SBS modifiers significantly improved
21 the anti-aging property of asphalt [8].

22 Siddiqui et al. studied the performance changes of aged SBS asphalt using

1 infrared spectra and thermal analysis, which showed the addition of SBS modifiers
2 into asphalt led to better anti-aging performance. Meanwhile, they tried to recycle
3 modified asphalt by adding new asphalt. Test results indicated that the recycling
4 technology of modified asphalt was feasible [9].

5 In order to evaluate the rheological properties and the viscosity-temperature
6 characteristics of asphalt/polyethylene blends, Vargas et al. obtained the activation
7 energy by solving the chemical reaction kinetics equation. And they acknowledged
8 that lower activation energies are preferred because viscosity changes slightly with
9 changing the same temperature amplitude [10]. Mturi et al. compared the differences
10 of rheological properties between aged base asphalt binder and aged modified asphalt
11 binder through rotational and oscillatory-derived viscosities test. The changes of aging
12 rate were also analyzed by Arrhenius relation based on chemical reaction kinetics
13 equation. They found that the Arrhenius relation can well describe the changes of
14 aging rate for the accelerated thermal ageing methods [11]. Vargas and Mturi both
15 treated the activation energy as a constant. However, aging influenced asphalt binder
16 chemistry and rheology significantly. These changes contain increases in amount of
17 large molecules, transformation of generic fractions and the formation of carbonyl
18 compounds and sulfoxides [12]. All these changes will lead to the change of asphalt
19 binder microscopic components and molecular structures, which will cause the
20 changes of activation energy and make the activation energy is no longer a constant
21 during the aging process.

22 Herrington et al. tested the changes in carbonyl area and verified the aging rate

1 meets the assumption of a first order dependence on oxygen concentration for rolling
2 thin film oven test and pressure aging vessel. The establishment of this assumption
3 proved the correctness of Arrhenius relation used to analyze aging rate during the
4 process of rolling thin film oven and pressure aging vessel [13]. Xin, et al. analyzed
5 the relationship between viscosity and carbonyl area tested by Fourier transform
6 infrared (FTIR) spectroscopy during oxidation aging process. A strong correlation is
7 observed between the rheological measurements and chemical analyses [14]. This
8 strong correlation demonstrated that the chemical composition and the rheological
9 properties of asphalt binder are complementary to each other. The flow state of
10 asphalt binder will be influenced by the variation of chemical composition during
11 oxidation aging process. It provides a strong argument for the Arrhenius relation
12 based on rheological properties. Therefore, we can use the flow state to characterize
13 the aging conditions of asphalt binder. The Arrhenius relation combined chemical
14 reaction kinetics with the principle of time temperature conversion, which was used to
15 analyze the aging mechanism in this study.

16 Research on aging mechanism of SBS modified asphalt can give a direction for
17 recycling of SBS modified asphalt pavement, so as to reduce the discard of waste SBS
18 modified asphalt mixture, save resources and protect the environment. In this study,
19 asphalt aging kinetics model was presented to further reveal the aging mechanism of
20 SBS modified asphalt and understand aging process from the perspective of chemical
21 reaction kinetics theory. The differences of aging mechanism between base asphalt
22 and SBS modified asphalt were also analyzed through micro components analysis and

gel permeation chromatography analysis.

2. Chemical reaction kinetics

Chemical reaction kinetics is a branch of physical chemistry discipline and its research object is a dynamic system. Reaction rate as an important indicator in chemical reaction kinetics was used to measure the speed level of chemical reaction. The relationship between chemical reaction rate and concentration of components is calculated by Eq.(1) [15].

$$r = f(C_A, C_B \cdots C_I \cdots) \quad (1)$$

Where r is reaction rate, $\text{mol} \cdot (\text{L} \cdot \text{h})^{-1}$; C_I is the concentration of I component, mol/L .

For most simple reactions and some compound reactions, the reaction rate equation is expressed as follows:

$$r = k C_A^p C_B^q \cdots \quad (2)$$

Where k is chemical reaction rate constant, h^{-1} ; p 、 q ...is respectively the reaction orders of corresponding components A 、 B The sum of each component reaction orders, n , is called total orders of reactions. And the reaction whose total orders is simple positive integers and zero is called as simple orders reaction. Usually asphalt aging can be thought as one orders reaction, which means asphalt aging rate is in direct proportion to the first power of reactants concentration, Eq. (3) [13,16]:

$$-\frac{dc}{dt} = kc \quad (3)$$

Where c is component concentration, mol/L ; t is reaction time, h . And Eq. (4) can be obtained through solving Eq. (3).

$$\ln c = B - kt \quad (4)$$

Where B is the integral constant. For the simple series reaction, its reaction rate equation can be easily established when the reaction series n and the reaction rate constant k are known. But the reaction rate constant k for one series reaction can be obtained from drawing $\ln c$ to t, and then the straight slope is equal to $-k$.

In order to describe the relationship between reaction temperature T and reaction rate constant k, the concept of activation energy is put forward and chemical reaction kinetics empirical formula is established by Arrhenius, Eq. (5).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

Where A is pre-exponential factor or frequency factor constant; R is molar gas constant, about 8.314J/(mol.K); T is absolute temperature, K; E_a is activation energy, J/mol.

According to the principle of chemical reaction kinetics, the activation energy refers to the energy barrier about activation of molecular. In Arrhenius's point of view, activation energy is the energy needed to transform the reactant molecules into activated molecules [17]. To some extent, the activation energy reflects the molecular composition and structure of reactants, which decides the chemical reaction rate. Eq. (5) also indicates that there are some connections between activation energy and temperature sensitivity. It reflects how much the chemical reaction rate changes when the test temperature increases or reduces to a certain degree. Generally, greater activation energy corresponds to a smaller chemical reaction rate at a given temperature. However, for the temperature sensitivity, the greater the activation

energy is, the worse the temperature sensitivity in a certain temperature interval is. Better temperature sensitivity means that the viscosity slightly with variation of the same temperature amplitude. Lower activation energies are preferred because the change of viscosity is smaller with changing the same temperature amplitude according to Equation (6).

The temperature dependence of the asphalt viscoelastic behavior, as indicated by the shift factors determined from the construction of master curves, may fit either the Arrhenius or the Williams–Landel–Ferry (WLF) equation. Within the temperature range studied in this work, the temperature dependence of the shift factor for all the systems studied is described by an Arrhenius-type equation fairly well, Eq. (6). According to the principle of time temperature conversion, the shift factor $\alpha(T)$ is defined as Eq. (7) [18].

$$\alpha(T) = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (6)$$

$$\lg \alpha(T) = \lg f_r - \lg f_0 \quad \alpha(T) = \frac{f_r}{f_0} \quad (7)$$

where $\alpha(T)$ is the shift factor at a temperature T relative to the reference temperature T_0 ; f_r is the shift frequency; f_0 is the frequency reference.

The complex modulus of asphalt under different temperature and frequency were obtained through frequency domain analysis. The principal curve of asphalt complex modulus was drawn based on the principle of time temperature conversion. The shift factor $\alpha(T)$ could be obtained by the principal curve according to Eq.(7). Then, a straight line could also be obtained by drawing a figure $\ln \alpha(T)$ to $1/T$. Comparing Eq.

(5) with Eq. (6), it can be found that the straight slope is equal to E_a/R and the intercept equals to $-E_a/(RT_0)$. So chemical reaction kinetics parameters based on the complex modulus of asphalt can be obtained. Then the dynamic characteristics of asphalt were analyzed during aging process according to chemical reaction kinetics.

3. Material preparation

Liaohe AH90 oil bitumen (an 80/100 pen grade bitumen, PG 64-22) and 791-SBS modifiers (one kind of SBS block copolymer modifiers and belongs to the linear structure with the ratio of styrene and butadiene being 30:70.) were selected as raw materials. The ductility at 5°C of asphalt binder after long-term aging process as the judge index was used to assess the SBS modifier decomposition conditions. If the ductility test at 5°C is hardly to proceed and the test specimens fracture directly, we think the SBS modifier degrade completely. In order to guarantee the SBS modifier to degrade completely during aging test, the SBS modifier content of modified asphalt was identified as 3% through indoor ductility test verification. The preparation steps are as follows. Firstly, add 3% (mass fraction) SBS modifier and a small amount of stabilizer into the melting base asphalt AH90. Then, at temperature of 170°C, the modified asphalt is subject to high speed shearing for 30 min and left to develop for 1 h. The basic performance indicators of AH90 oil bitumen and SBS modified asphalt (PG 70-22) are shown in Table 1. In order to compare similarities and differences between base asphalt and SBS modified asphalt, aged AH90 asphalt and aged SBS modified asphalt were respectively prepared by carrying out laboratory short-term and

- 1 long-term aging process: rolling thin film oven test (RTFOT, standard ASTM D2872)
- 2 and pressure aging vessel (PAV, standard ASTM D6521).

3 Table1. Test results of base asphalt and SBS modified asphalt

Tests	Penetration (25 °C) (0.1mm)	Softening Point (°C)	Softening point difference (°C)	Ductilit y (cm)	Viscosity (135°C) (mPa.s)	$G^*/\sin\delta$ (64°C) (KPa)	Creep stiffness $S(-18\text{ }^{\circ}\text{C})$ (MPa)	Creep rate m (-18°C)
Test methods	ASTM D 5	ASTM D 36	ASTM D5976	ASTM D113	ASTM D 4402	AASHT O T 315	ASTM D 6648	
AH90	84	42.5	-	>100 (15°C)	410	1.1	294	0.34
SBS modified asphalt	74	51.5	1	41(5°C)	1435(shea r thinning)	2.1	267	0.35

4

5 4. Testing methods

6 4.1 Dynamic shear rheology test (AASHTO T 315)

7 In order to draw the principal curves of complex modulus of asphalt under different
8 aging states, frequency sweeping of asphalt under different aging states at different
9 temperature was necessary. DSR II type dynamic shear rheometer (DSR) was adopted
10 in this experiment. Complex modulus (G^*) and phase angle (δ) of asphalt were
11 measured under six kinds of temperature 52°C、58°C、64°C、70°C、76°C、82°C,
12 respectively. According to AASHTO MP1 test method, 1mm thickness asphalt sample
13 was placed in the middle of two parallel disc with the dimension of 25mm. Complex
14 modulus (G^*) and phase angle (δ) were calculated through measuring the applying
15 torque with the bottom plate fixed and the upper plate moving at different shear

frequencies[19]. The strain control mode was used in this test.

4.2 Component analysis

The appropriate component contents are the basic guarantee of asphalt performance. To explain the results of chemical reaction kinetics, component analysis method was used to study the change of each component of asphalt under different aging conditions. The components of AH90 asphalt and SBS modified asphalt were analyzed by means of four component analysis based on technical specification (standard ASTM D4124). Asphalt colloidal unstable index, I_c , is calculated according to Eq. (8). Colloidal unstable index reflects the stability of structural system of asphalt performance. A greater colloidal unstable index corresponds to a more unstable colloid structure [20].

$$I_c = (S + A_s) / (R + A_r) \quad (8)$$

where S (%) is the saturates content of asphalt, A_s (%) is the asphaltene content of asphalt, R (%) is the resins content of asphalt, and A_r (%) is the aromatics content of asphalt.

4.3 Gel permeation chromatography (GPC)

GPC is a method of separation according to the molecular size when polymer solution goes through a column composed of special porous fillers. GPC analysis is commonly used to determine the molecular weight and molecular weight distribution. Gel permeation chromatography analyzer is mainly composed of solvent, solvent pump storage, solution injection control valve, GPC column, detector, waste solution

and solvent storage pool, etc [21, 22]. In order to better explain the analysis result of chemical reaction kinetics, Malvern ViscotekHT-GPC type gel chromatography permeameter is adopted to analyze the distribution of micro molecular of asphalt under different aging conditions.

Most polymers are composed of different size molecules with the same link structure, but with different molecular chain length. The molecular weight of polymer is actually a statistical average of molecular weight of a variety of different sizes polymer. Each polymer has its own molecular weight distribution due to the poly dispersion of molecular weight. Common average molecular weight contains number-average molecular weight, M_n , and weight-average molecular weight, M_w , Eqs. (9 and 10). Distribution width of polymer molecular weight is a quantitative description of polymer dispersing degree, which is described using dispersion M_w/M_n [23]. From the results of GPC, we can obtain the distribution of polymers with different molecular weight according to leaching volume. Because the mole fraction is proportional to the leaching volume for the polymer solution, M_n and M_w can be automatically calculated by the computer based on the leaching volume and the leaching net mass at different time [24].

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \sum N_i M_i \quad (9)$$

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \sum W_i M_i \quad (10)$$

where n is mole number of molecular in mol, w is the weight of molecular in g, M is molecular weight in kD, N is the mole fraction and W is the weight fraction.

1

2 **4.4 Grey entropy theory analysis**

3 Grey entropy correlation analysis, as an important part of grey theory system, is an
4 effective method for information system analysis. It is also the cornerstone of the grey
5 system analysis, forecasting and decision-making. Grey entropy theory is used to
6 determine the correlation degree among different factors through calculating the grey
7 correlation degree and the grey entropy correlation degree. The main factors and the
8 secondary factors are divided by analyzing the relationship between the various
9 factors and the system development situation, which play a positive role in guiding
10 the system development [25].

11 Therefore, the grey correlation entropy analysis method was introduced in this
12 paper. In order to find out the main factors influencing the activation energy, the
13 correlation extent between activation energy and asphalt microscopic components,
14 asphalt molecular structure was analyzed based on grey entropy theory analysis
15 method. And analyzing the main factors affecting activation energy of asphalt can not
16 only help us understand the aging mechanism of asphalt from micro level, but also
17 provide theoretical and technical supports for recycling of SBS modified asphalt
18 pavement.

19 Fig. 1 provides a flow chart of calculation steps about grey entropy theory analysis.
20 The steps of comprehensive evaluation using grey correlation entropy analysis
21 method are as follows [26]:

22 Step 1. Determine the evaluation system and collect evaluation data according to the

1 evaluation purpose. For example: There are n factors, each factor has m levels, and
 2 these n×m data can form a matrix, Eq.(11).

$$3 \quad (X'_1, X'_2, \dots, X'_n) = \begin{bmatrix} x'_1(1) & x'_2(1) & \cdots & x'_n(1) \\ x'_1(2) & x'_2(2) & \cdots & x'_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ x'_1(m) & x'_2(m) & \cdots & x'_n(m) \end{bmatrix} \quad (11)$$

4 Step 2. Determine the reference data sequence, Let $X'_0 = (x'_0(1), x'_0(2), \dots, x'_0(m))^T$, and
 5 the others are compare sequence. Dimensionless processing of data is written down as
 6 follows, Eq. (12): $X_i = (x_i(1), x_i(2), \dots, x_i(m))^T, i = 1, 2, \dots, n$.

$$7 \quad x_i(k) = \frac{x'_i(k)}{x'_i(1)} \quad i=0, 1, \dots, n; k=1, 2, \dots, m \quad (12)$$

8 Step3. Determine $\min_i \min_k |x_0(k) - x_i(k)|$ and $\max_i \max_k |x_0(k) - x_i(k)|$.
 9 $\min_i \min_k |x_0(k) - x_i(k)|$ is the minimum difference and $\max_i \max_k |x_0(k) - x_i(k)|$ is the
 10 maximum difference. Then calculate the correlation coefficient $\xi_i(k)$ and grey
 11 correlation degree r_{0i} according to Eqs. (13) and (14).

$$12 \quad \xi_i(k) = \frac{\min_i \min_k |x_0(k) - x_i(k)| + \rho \max_i \max_k |x_0(k) - x_i(k)|}{|x_0(k) - x_i(k)| + \rho \max_i \max_k |x_0(k) - x_i(k)|} \quad (13)$$

$$13 \quad r_{0i} = \frac{1}{m} \sum_{k=1}^m \xi_i(k) \quad (14)$$

14 Where ρ is resolution coefficient. The smaller the value of ρ is, the greater difference
 15 of correlation coefficient has, the stronger ability of distinguish becomes. And the
 16 value of ρ usually assumes as 0.5.

17 Step 4. Construct grey correlation degree sequence $R_i = \{\xi_i(k) | k=1, 2, \dots, m\}$.

18 Mapping processing is made for R_i and the mapping T: $R_i \rightarrow P_i$. T is called as

19 distribution mapping of the correlation coefficient $\xi_i(k)$, which meets Eq. (15), and p_h

1 is called as the density value of distribution.

$$2 \quad p_h \triangleq \frac{\xi_i(h)}{\sum_{k=1}^m \xi_i(k)} \quad p_h \in P_i, h = 1, 2, \dots, m \quad (15)$$

3 Step 5. Calculate grey correlation entropy and grey entropy correlation degree
4 according to Eq. (16) and Eq. (17) .

$$5 \quad H(R_i) = - \sum_{h=1}^m p_h \ln p_h \quad (16)$$

$$6 \quad E_r(X_i) = \frac{H(R_i)}{H_m} \quad (17)$$

7 Where $H(R_i)$ is the grey correlation entropy of X_i ; $E_r(X_i)$ is the grey entropy
8 correlation degree; H_m is the maximum of grey correlation entropy and $H_m = \ln m$. The
9 correlation between reference data sequence and compare data sequence becomes
10 stronger when grey entropy correlation degree $E_r(X_i)$ increases.

11 Step 6. Grey correlation degree is a measure of sequence proximity, and grey
12 entropy correlation degree is a measure of sequential equilibrium degree, so
13 equilibrium proximity of sequence is established by the product of grey correlation
14 degree and grey entropy correlation degree, Eq. (18) .

$$15 \quad w_i = E_r(X_i) \times r_{0i} \quad (18)$$

16 Where w_i is the equilibrium proximity between reference data sequence and the i^{th}
17 compare data sequence. The greater the value of w is, the more balanced relationship
18 of evaluation object has and the better correlation the reference object has.

Fig.1 The procedure of calculation steps about grey entropy theory analysis

5. Test results and discussion

5.1 Aging reaction kinetics analysis based on complex modulus

The complex modulus of asphalt under different aging conditions was tested by dynamic rheological shear apparatus. The complex modulus of asphalt with different aging states showed a similar change rule. The complex modulus increased with the increase of frequency, but decreased with the increase of temperature. Based on time temperature equivalence principle, asphalt complex modulus principal curve was obtained by moving the complex modulus curves of asphalt under different temperature and frequencies to the reference temperature at 64°C. The complex modulus principal curves of original AH90 and original SBS modified asphalt were

1 shown in Fig.2 and Fig.3, respectively. The shift factors $\alpha(T)$ of asphalt under
 2 different temperature can be calculated according to Eq.(7). And results were shown
 3 in Table 2.

4
5 Fig.2 The master curve of complex modulus of base asphalt

6
7 Fig.3 The master curve of complex modulus of SBS modified asphalt

Table2. The calculation results of shift factors $\alpha(T)$

Asphalt types	Temperature ($^{\circ}\text{C}$)					
	52	58	64	70	76	82
AH90-Ori	7.296703	2.263736	1	0.56044	0.230769	0.131868
AH90-RTFOT	6.311321	2.490566	1	0.429245	0.198113	0.099057
AH90-PAV	6.397059	2.500000	1	0.431373	0.200980	0.102941
SBS modified asphalt-Ori	4.961268	2.228873	1	0.464789	0.232394	0.130282
SBS modified asphalt- RTFOT	4.875728	2.23301	1	0.423301	0.312621	0.200000
SBS modified asphalt- PAV	4.804074	1.787745	1	0.433953	0.142932	0.071307

According to Arrhenius equation Eq.(6), draw a line $\ln\alpha(T)-1/T$, whose slope is equal to E_a/R and intercept is equal to $-\ln A$. The regression relation between $\ln\alpha(T)$ and $1/T$ of original base asphalt and original SBS modified asphalt are shown in Fig.4 and Fig.5, respectively. Then the activation energy E_a and pre-exponential factor A of asphalt under different aging states were obtained as shown in Table 3.

Fig.4 The relationship between $\ln\alpha(T)$ and $1/T$ of base asphalt

Fig.5 The relationship between $\ln \alpha (T)$ and $1/T$ of SBS modified asphalt

Table3. The chemical reaction kinetic parameters of asphalt

Asphalt types	Activation energy E_a (kJ/mol)	pre-exponential factor $\ln A$	correlation coefficient R^2
AH90-Ori	126.697	45.024	0.9936
AH90-RTFOT	133.905	47.721	0.9993
AH90-PAV	133.240	47.472	0.9989
SBS modified asphalt-Ori	117.959	42.053	0.9989
SBS modified asphalt- RTFOT	104.698	37.247	0.9814
SBS modified asphalt- PAV	133.772	47.923	0.9952

In the research of aging process of asphalt, activation energy is always regarded as a constant. However, it has been found that activation energy of SBS modified asphalt is various under different aging stages from the calculation in Table 3. Activation energy of SBS modified asphalt after long-term aging increased by 27.8% compared

1 with the asphalt after short-term aging.

2 From Eq. (5), it is not difficult to find that the greater the activation energy of
3 asphalt is, the smaller the chemical reaction rate shows and the worse the temperature
4 sensitivity displays. The results of Table 3 show that the aging rate of asphalt under
5 PAV aging condition becomes smaller and the temperature sensitivity becomes worse
6 due to greater activation energy. This is mainly because SBS modified asphalt
7 becomes stiffer and gradually loses activated ingredients after long-term aging. Then
8 the aging rate is restricted to a given temperature. In addition, greater activation
9 energy means a greater chemical reaction rate gradient when the test temperature
10 increases or reduces to a certain degree. Then the features of stiffer will limit the
11 adaptability of asphalt in a certain temperature interval. Therefore, the temperature
12 sensitivity becomes worse, though the aging rate of SBS modified asphalt becomes
13 smaller after long-term aging.

14 Table 3 illustrates that activation energy of AH90 bitumen increases with deepening
15 of aging. However, activation energy of original asphalt decreases and temperature
16 sensitivity increases with the addition of SBS modifier. This is mainly because SBS
17 modifier will disperse into micron grade granules under the high speed shearing
18 action, which increases the specific surface area of SBS modifier. Swelling and
19 plasticizing effects of SBS modifier change the colloidal structure after absorbing the
20 small molecules in asphalt, and three-dimensional network of SBS limits the
21 movement of asphalt colloid particle. As a result, the SBS needs to absorb more
22 energy when the SBS itself deforms or moves [27]. But in the aging process,

1 activation energy of SBS modified asphalt decreases firstly, then increases, and finally
2 closes to AH90 matrix asphalt. It may be the consequence of synthetic action between
3 medium-sized molecules produced in the aging process and three-dimension network
4 structure under the action of RTFOT, which contribute to a better colloidal stability.
5 However, with further aging of SBS modified asphalt, SBS continued disintegrating
6 and producing much small molecule structures, leading to the temperature sensitivity
7 of SBS modified asphalt closing to the base asphalt after long-term aging.

8 In order to further reveal the nature of activation energy change during asphalt
9 aging, two Microscopic analysis methods, component analysis and GPC analysis,
10 were used to study the change of asphalt composition and molecular structure during
11 the process of aging.

12

13 **5.2 Component analysis results**

14 Fig.6 represents four component analysis results of AH90 and SBS modified
15 asphalt on different aging stages. Compared with AH90 asphalt, the saturate content
16 significantly decreased along with the addition of SBS modifier into original asphalt.
17 Additionally, the change of aromatics content was not obvious, the resins and
18 asphaltene content increased and the colloidal unstable index decreased obviously for
19 SBS modified asphalt binder. It is the changes in microscopic components that lead to
20 the significant differences of rheological properties and anti-aging performance for
21 SBS modified asphalt compared with AH90 asphalt.

Fig.6 Components analysis of asphalt with different aging stages

Fig.6 indicates that saturate content and aromatics content of base asphalt will significantly decline and asphaltene content will substantially improve during the aging process. Both the two phenomena will lead to the increase of the colloidal unstable index and the activation energy. When SBS modified asphalt experiences

1 short-term aging, the saturates content will slightly decrease and the resins content
2 will substantially increase because of further fusion reaction between asphalt and
3 modifier. Therefore, the colloidal unstable index of SBS modified asphalt under
4 RTFOT aging condition will substantially decrease , which will lead to a reduction of
5 activation energy and an improvement of temperature sensitivity. However, after
6 long-term aging, the saturates content of SBS modified asphalt will increase
7 enormously resulting from the degradation of SBS modifiers. Furthermore, the vast
8 saturate content and aromatics content will be transformed into asphaltene content,
9 resulting in a substantial increase caused by the unstable colloidal index of SBS
10 modified asphalt. All these varying patterns of components analysis are consistent
11 with the conclusion of the literature [28]. These also explain why the activation
12 energy of SBS modified asphalt after long-term aging basically approach to base
13 asphalt and even more lose the modification effects.

14

15 **5.3 GPC analysis results**

16 GPC is a kind of technology used to measure relative molecular mass. Fig.7 and
17 Fig.8 respectively shows the GPC chromatograms of base asphalt AH90 and SBS
18 modified asphalt under different aging stages. The area under the curve represents
19 100% of the binder's molecules injected into the GPC system. Researchers have
20 classified binder constituents into several groups by molecular size [29-30]. In this
21 study, a chromatographic profile was partitioned into 9 slices, which were further
22 divided into three parts, namely large molecular size (LMS), medium molecular size

1 (MMS) and small molecular size (SMS), corresponding to slices with the sizes of 1-4,
 2 5-7, and 8-9, respectively. Defining LMS part as front 4 slices is based on the
 3 previous study, in which LMS was defined as the area from elution start to the elution
 4 time slightly over 1/3 of total elution time [31]. The elution of sample is detected in
 5 milli-volt (mV) as shown in Fig. 7 and Fig. 8. Relative quantity (the area under the
 6 curve) by percentage of each part to for asphalt binder under different aging states
 7 was respectively calculated, as shown in Table 4.

8

9

10 Fig. 7 GPC chromatogram of base asphalt binder AH90

Fig. 8 GPC chromatogram of SBS modified asphalt binder

Table 4. The results of GPC analysis

Asphalt types	LMS(%)	MMS(%)	SMS(%)	Mn	Mw	d
AH90-Ori	6.55	56.72	36.73	666.1	3855	5.787
AH90-RTFOT	10.00	56.27	33.73	735.7	4510	6.130
AH90-PAV	16.82	57.32	25.86	768.7	4872	6.338
SBS modified asphalt-Ori	8.55	59.82	31.63	835.2	14794	17.713
SBS modified asphalt- RTFOT	8.60	60.57	30.83	949.7	12314	12.996
SBS modified asphalt- PAV	9.53	61.87	28.60	988.5	11137	11.267

Note : Mn—number-average molecular weight; Mw—weight-average molecular weight; d—dispersion.

The results of Fig.7 show that the small molecules of base asphalt gradually transform

1 into large molecules during the aging process. And in Fig.8, distinct double peak
2 phenomenon can be found in the GPC chromatogram of original SBS modified
3 asphalt. This double peak are also detected by the references [23,24]. According to the
4 principal of GPC, the first elution content (the first peak of Fig.7 16ml-22ml) is SBS
5 modifier which has bigger molecular weight, and the second elution content (the
6 second peak of Fig.8) is the small molecular substances in asphalt. SBS modifier will
7 degrade into small molecules with the deepening of aging, which will lead to an
8 increase of molecular composition with the leaching volume at 22ml-24ml. And in
9 order to understand the molecular weight changes of SBS modifier, the big molecular
10 substances (elution content 16ml-22ml) were separated and calculated, as shown in
11 Table 5.

12 Table 5. Molecular weight calculation results of SBS modifier

Asphalt types	Mn	Mw	d
SBS modified asphalt-Ori	159321	186328	1.169513
SBS modified asphalt-RTFOT	118938	153470	1.290336
SBS modified asphalt-PAV	69153	110082	1.591862

13
14 Generally the number-average molecular weight reflects the change trend of medium
15 or small molecules in asphalt, while the weight-average molecular weight reflects the
16 content of macromolecular in asphalt. The results of Table 4 show that the
17 number-average molecular weight of SBS modified asphalt increases, but the
18 weight-average molecular weight constantly decreases with the deepening of aging,
19 which mainly results from the splitting of SBS modifiers. The results of Table 5

1 illustrate that the decreasing trend of molecular weight of SBS modifier is obvious in
2 the process of aging. The weight-average molecular weight of SBS modifier
3 respectively decreases by 18% and 41% after short-term aging and long-term aging.
4 The number-average molecular weight of SBS modifier after long-term aging is close
5 to half of its original value, which means SBS modifier has suffered serious
6 degradation and it seriously affects the SBS modified asphalt properties. All these
7 phenomena are consistent with the conclusion of the literature [20]. However,
8 compared with the number-average molecular weight, the change of weight-average
9 molecular weight of base asphalt is more sensitive. The asphalt aging reaction mainly
10 includes dissociation and condensation. The condensation will generate more and
11 more macromolecular structure, which lead to greater weight-average molecular
12 weight of base asphalt, while the dissociation will produce more and more small
13 molecules with low boiling point. However, the condensation plays a leading part in
14 the aging process of base asphalt and only small amounts of dissociation will occur,
15 which finally leads to increase the dispersion of base asphalt after aging.

16

17 **5.4 Grey entropy theory analysis results**

18 According to the grey correlation entropy analysis method, the activation energies
19 (X_0) is used as reference sequence in this paper. Saturates content (X_1), asphaltenes
20 content(X_2), resins content(X_3), aromatics content(X_4), colloidal unstable index (X_5),
21 large molecular size structure content(X_6), medium molecular size structure
22 content(X_7) and small molecular size structure content(X_8) served as compare

1 sequence. Then the influence of micro components and molecular structures on
 2 activation energy was analyzed as the six steps in section 4.4. The results of grey
 3 correlation entropy analysis are shown in Table 6.

4 Table 6. The results of grey correlation entropy analysis

Compare sequence	Grey correlation degree r_{0i}	Entropy correlation $E_r(X_i)$	Equilibrium proximity extent w_i
Saturates content (X1)	0.90409	0.99827	0.90253
Asphaltenes content (X2)	0.73575	0.98718	0.72632
Resins content (X3)	0.88837	0.99687	0.88560
Aromatics content (X4)	0.86366	0.99844	0.86231
Colloidal unstable index (X5)	0.90752	0.99881	0.90645
LMS structure content (X6)	0.64740	0.97453	0.63091
MMS structure content (X7)	0.90733	0.99784	0.90537
SMS structure content (X8)	0.86036	0.99458	0.85569

5
 6 Through comparing the equilibrium proximity w_i according to Table 6, it can be
 7 shown that $X5 > X7 > X1 > X3 > X4 > X8 > X2 > X6$. The results indicate that the factors
 8 have closely correlation with activation energy include colloidal unstable index,
 9 medium molecular size structure content and saturates content. It is conducive to
 10 reduce activation energy and improve asphalt temperature sensitivity with the
 11 decrease of colloidal unstable index and saturates content, the increase of medium
 12 molecular size structure content. The addition of SBS modifier not only reduces the
 13 saturates content but also improves the content of MMS structure, which decreases the
 14 activation energy of SBS modified asphalt and enhances the stability of the asphalt.

1 But activation energy of SBS modified asphalt has changed under aging process. The
2 variation of saturates content of SBS modified asphalt during short-term aging is
3 reduced. In addition, the formation of MMS structure due to the degradation of SBS
4 modifiers decreases the activation energy of SBS asphalt after short-term aging and
5 improves the temperature sensitivity. However, after long-term aging, the saturates
6 content of SBS modified asphalt increases significantly and the resins content
7 decreases obviously. As a consequence, the activation energy of SBS modified asphalt
8 increases, the temperature sensitivity of SBS modified asphalt tend to be closer to
9 base asphalt. Therefore, the modification effect of SBS modified asphalt is not evident
10 after long-term aging.

11

12 **6. Conclusions**

13 This paper analyzed the activation energy of asphalt under different aging
14 conditions based on the principle of chemical reaction kinetics. Then component
15 analysis and GPC were respectively used to study the change of asphalt composition
16 and molecular structure during aging process. In addition, the correlation between
17 activation energy and asphalt microscopic components, asphalt molecular structure
18 was also analyzed based on grey entropy theory analysis method. The following
19 conclusions can be drawn.

20 (1) The calculation results of activation energy illustrate that the activation energy of
21 asphalt is not as generally believed as a constant, but it changes along with aging. The
22 activation energy of base asphalt will increase during aging process. However, for
23 SBS modified asphalt, the activation energy will decrease firstly and then increase.

1 Therefore, the activation energy can be used to evaluate the aging degree of SBS
2 modified asphalt as one evaluation index.

3 (2) The aging of SBS modified asphalt is formed by both aging of base asphalt and
4 SBS modifier. In the process of aging, SBS modifiers are gradually degraded into
5 small molecules and SBS modified network structures gradually lose effectiveness.
6 SBS modified asphalt under different aging degree shows different activation energy
7 value because of the differences of composition and molecular structure. SBS
8 modified asphalt after short-term aging will degrade to more medium molecular size
9 structures, which make the activation energy become lower. But the activation energy
10 of SBS modified asphalt after long-term aging increases and temperature sensitivity
11 approximate to base asphalt due to the significant increase of saturates content and
12 decrease of resins content. The SBS modifiers after long-term aging have almost
13 degraded completely and lost modification effect.

14 (3) The factors that have closely correlation with activation energy contain colloidal
15 unstable index, medium molecular size structure content, saturates content and resins
16 content. The activation energy is reduced and asphalt temperature sensitivity is
17 improved with the increase of medium molecular size structure content, the decrease
18 of saturates content and the increase of resins content. This also explains why
19 activation energies are different under different aging states.

20 (4) SBS modified asphalt under serious aging condition will lose modification effect,
21 which will make the activation energy of SBS modified asphalt approximate to
22 ordinary unmodified asphalt. Therefore, SBS modified asphalt under serious aging

condition is unsuitable for directly modified recycling without the second modification. However, SBS modified asphalt under serious aging condition can be applied to recycled asphalt mixture as aged ordinary unmodified asphalt. It is a good recommendation that the aging degree of SBS modified asphalt should be evaluated before recycling SBS modified asphalt mixture.

(5) However, results and analyses provided in this paper are only based on one base asphalt binder and one SBS modified binder. A further study on more kinds of asphalt will be the focus of our next work.

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