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Regeneration mechanisms of aged SBS modified asphalt from RAP materials: Molecule structure, morphology, phase transition, and interface adhesion characteristics

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ABSTRACT

In this study, the environmentally friendly rejuvenators with waste thermal conductive oil, polymer, and the interfacial reinforcing agent were prepared. And the influence of the different rejuvenators on the rejuvenation mechanisms of aged SBS modified asphalt was characterized by different scales including the molecule structure, morphology, phase transition and interface adhesion characteristic, and macro performance. The results show that the thermal-oxidative aging process increases the molecular weight of asphalt, promotes the SBS phase to agglomerate, and decreases the high and low temperature performance, thermal stability, and adhesion. When the rejuvenator was added, the molecular weight distribution of asphalt binders can be improved, while adding the regenerant-II can supplement the SBS modifier and reform the cross-linking structure. Furthermore, the regenerant-II has a better recovery effect on the morphology structure and resumes the thermal behavior. And then softening point and ductility can be recovered by 89.7% and 94.8% of the original SBS modified asphalt. Under the action of the interfacial reinforcing agent, the regenerant-III could increase the adhesion work to 95.49% of the original SBS modified asphalt.

1. Introduction

Recently, asphalt binders are widely used in road pavement construction due to their excellent performance, and a comparatively perfect transportation network has been formed. According to statistics, there are annually more than one billion tons of asphalt mixtures applied on the pavement worldwide [1,2]. Therefore, how to realize the efficient utilization of vast amounts of aggregates and asphalt binders is very important for sustainable development. During the long-term service period, the asphalt pavement would appear some permanent diseases such as rutting, cracking, water damage, etc, by the challenge of the extreme weather, ultraviolet radiation, and traffic loads, which have negative effects on the driving comfort and traffic safety [3-5]. Thus, above asphalt road pavement needs to be maintained or reconstructed, and a large amount of reclaimed asphalt pavement (RAP) materials are produced and stacked into mountains. However, the RAP materials stored in an open field for a long time would cause land resource occupation, air pollution, and water pollution (Fig. 1). In addition, if the RAP materials have not been disposed of and utilized directly in the traditional technology, they must be downgraded and used in the lower-level road or structures [6]. And then recycling technology, including hot recycling technology, cold recycling technology, in-place recycling technology, and in-plant recycling technology have developed, which have different RAP content, regeneration effect, and energy consumption [7]. Hence, how to achieve the efficient recycling of RAP materials is a bright spot in the field of pavement engineering and an effective way for sustainable development and environmental protection [8].

According to recycled asphalt mixture, although there are just 3%-5% of asphalt binders in RAP materials, the regeneration of aged asphalt binder in RAP plays an important role in utilizing the recycled asphalt mixture, and then adding rejuvenator is an effective method to restore the thermal–mechanical and rheological of the binders, which could improve the service life of asphalt pavement [9,10]. During the service of asphalt pavement, the asphalt binder is continuously aged by the

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thermal oxygen and ultraviolet radiation, that is, the light components (aromatics) are decreasing, and the heavy components (asphaltenes) are increasing, which will lead to the hardening and brittle of asphalt [11-13]. Nowadays, the ordinary means of asphalt regeneration is to replenish the light components lost during aging, and restore its chemical composition, physical and rheological properties [14]. For example, adding waste lubricating oil can significantly improve the low-temperature ductility of aged bitumen. And when the waste lubricating oil content is 6%, the properties of rejuvenated asphalt can meet the technical standards of the original asphalt [15]. Otherwise, the physical and rheological properties of the aged asphalt can be restored and meet the technical specifications of its original asphalt when the optimum amount of waste vegetable oil was added. Meanwhile, waste edible vegetable oil can also improve the aging resistance, rutting resistance, and elastic recovery properties of the aged asphalt [16]. As stated above, many waste materials, such as waste vegetable oil and waste engine oil, have been used to prepare the rejuvenators for the RAP materials, achieving high economic benefits while taking into account the friendly protection of the environment [17]. Meanwhile, most of the rejuvenators were invented for aged base asphalt. As we all know, the upper and middle layers of high-grade asphalt pavement consist of SBS modified asphalt in China [18]. However, when the binder in RAP materials is aged SBS modified asphalt, the above-mentioned rejuvenators cannot meet the requirements. As we all know, the SBS modified asphalt samples are prepared by base asphalt, that is to say, the SBS modified asphalt is composed of the base asphalt, SBS modifier, compatibilizer, stabilizer, etc. Meanwhile, they have different properties, such as softening point, ductility, storage stability, and so on. What's more, there are difference in the aging process. Compared to aged asphalt, the process of SBS modified asphalt aged includes the aging of SBS and asphalt. The aging process will destroy the cross-linked structure of SBS in SBS modified asphalt, which is also the main reason for decreasing the performance of SBS modified asphalt. More vividly, the aging process of SBS modified asphalt in service is shown in Fig. 2 [19]. In addition, the common rejuvenator can only rejuvenate base asphalt, and replenish some missing light components in the aged asphalt, but cannot repair the cross-linked structure of SBS modified asphalt and improve the interface adhesion characteristics [20].

The cross-linked structure formed by chemical reaction plays a crucial role in improving the performance of SBS modified asphalt mixtures[21], so how to restore the cross-linked structure for the aged SBS modified asphalt system is the focus in the research [22]. It is found that the bond of -C = C- in the SBS polymer is prone to break under the thermal-oxidative aging process, and the reactive functional groups tend to generate carbonyl and sulfoxide groups, leading to a significant increase of oxygen content in SBS modified asphalt [23]. Han [24] pointed out that the cross-linked structure of SBS can be reconstructed by hexamethylene diisocyanate (HDI) and toluene-2,6-diisocyanate (TDI), while the rheological properties and basic performance of SBS modified asphalt can be restored by adding the common rejuvenator. However, the HDI and TDI have a limited ability to restore the cross-linked structure, and the adhesion of the rejuvenated asphalt was not considered, which did not have a good effect on the recovery of the recycled asphalt mixture. Simultaneously, there are many side reactions due to the two substances being extremely reactive, which are also highly toxic and harmful to the environment and humans. Therefore, exploring an effective method or material to realize the recovery of cross-linked network structure and interfacial adhesion is a hot topic in SBS modified asphalt regeneration.

Therefore, in order to comprehensively improve the performance of recycled SBS modified asphalt mixture, the highly efficient and environmentally friendly rejuvenators with waste thermal conductive oil, polymer, interfacial reinforcing agent, etc., were prepared in this paper. And the regenerant-II with the non-interfacial reinforcing agent and regenerant-III with the interfacial reinforcing agent were selected to explore the change of adhesion for SBS modified asphalt. The influence of the different rejuvenators on the rejuvenation mechanisms of aged SBS modified asphalt was characterized by different scales, which included the molecule structure, morphology, phase transition and interface adhesion characteristic, and macro performance investigated. Among them, the gel permeation chromatography test (GPC) was used to evaluate the change in the molecular weight distribution of SBS modified asphalt before and after regeneration. The morphology including the SBS phase dispersion state can be characterized by the Fluorescence microscopy (FM). And the differential scanning calorimetry test (DSC) can be used to evaluate the thermodynamic behaviors of SBS modified asphalt. Meanwhile, the influence of interfacial reinforcing agent on the adhesion of asphalt mixture was analyzed by the contact angle test. And then the conventional properties tests were used to investigate the the regeneration effect of SBS modified asphalt from a macro perspective. And the conclusions are significant for improving the regeneration effect of aged SBS modified asphalt, increasing the RAP content, and controlling the quality of regeneration asphalt pavement.

2. Materials and methods

2.1. Materials

2.1.1. Asphalt and SBS modified asphalt

The characteristics of SBS modified asphalt are affected by the base asphalt, then the base asphalt, namely Ssangyong 70# produced by Korea Asphalt Plant was selected to prepare SBS modified asphalt

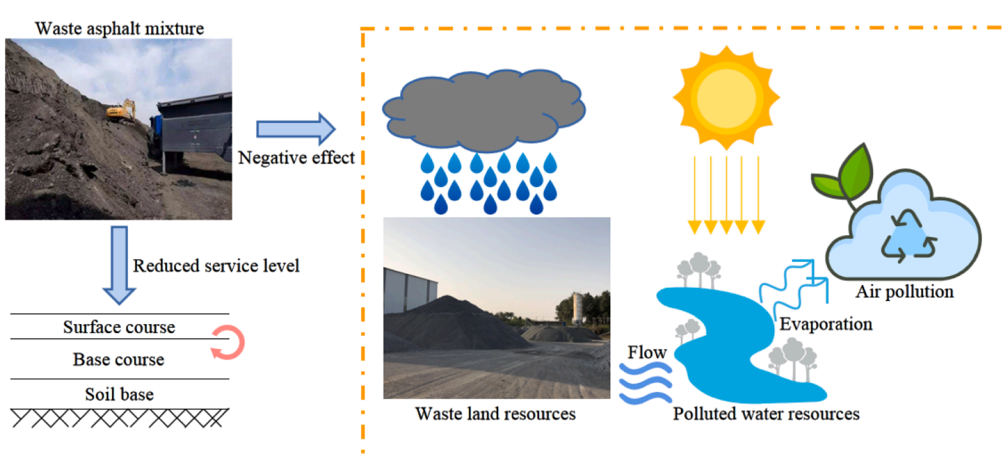

Fig. 1. Disadvantages of RAP materials storage in the open filed.

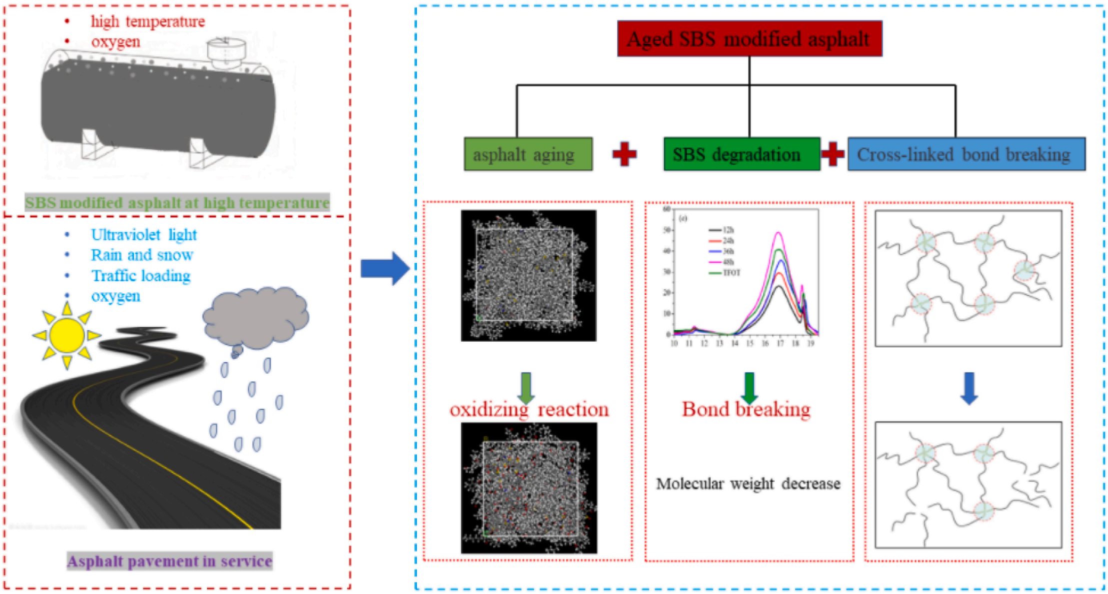

Fig. 2. The Aging process of SBS modified bitumen in asphalt pavement or storage in high temperatures.

samples, and the properties of the base asphalt are shown in Table 1.

And the SBS modified asphalt samples manufactured by Nantong Tongsha Asphalt Technology Co., Ltd in Jiangsu Province were employed, and this product was widely used in Highway maintenance engineering. The properties of the SBS modified asphalt are presented in Table 2.

2.1.2. Rejuvenating agents

As for the aged SBS modified asphalt, the self-made regenerant-II and regenerant-III were used to characterize the rejuvenation mechanisms, which were including the waste thermal conductive oil (alkyl naphthalene thermal oil), polymer (styrene–butadienestyrene co-polymer), interfacial reinforcing agent (interfacial reinforcing agent), etc. Among them, in order to evaluate the change of adhesion for SBS modified asphalt, the regenerant-III consisted of the interfacial reinforcing agent compared to the regenerant-II. Meanwhile, they are highly efficient and environmentally friendly rejuvenator. Moreover, the regenerant-I, with high content of aromatics for the aged base asphalt, was selected as a control sample, which was produced by a chemical company in Jiangsu. And the performance of the rejuvenating agents are listed in Table 3.

2.2. Preparation of the aged SBS modified asphalt samples

Traditionally, the aged asphalt is obtained from the RAP materials by extraction test. However, aged asphalt includes some impurities such as mineral fines, trichloroethylene, etc., which have a negative effect on performance. Meanwhile, the aged asphalt sample is less than 100 g every time, and it is not enough for conventional properties testing [25]. Therefore, to obtain the appropriate aged SBS modified asphalt, the thin film oven test was employed in this section, and the aging time, including 5 h, 7 h, 9 h, 11 h, and 13 h were investigated at the aging temperature of 163℃. And the testing results are listed in Table 4. It can be found that when the aging time is 9 h and the aging temperature is 163℃, the performance of samples is similar to that of the aged SBS modified asphalt from the RAP materials with 7–10 years of service life.

Table 1
Properties of base asphalt.

Items		Result	Specification value	Test methods (JTG E20)
Penetration/ (0.1 mm, 25℃)		72	60 ~ 80	T0604
Softening point/°C		47.6	≥46	T0606
Ductility/ (cm,15℃)		126	≥100	T0605
Flash point/°C		324	≥260	T0611
Solubility/%		99.8	≥99.5	T0607
TFOT (163 °C, 5 h)	Mass loss/%	0.163	±0.8	T0609
	Penetration ratio/%	64.1	≥61	T0604
	Ductility/ (cm,15℃)	38.5	≥15	T0605

Table 2
Properties of SBS modified asphalt.

Items		Result	Specification Value	Test methods (JTG E20)
Penetration/ (0.1 mm, 25℃)		54	40 ~ 70	T0604
Ductility/ (cm, 5℃)		32.6	≥25	T0605
Softening point/°C		80.7	≥70	T0606
60℃ dynamic viscosity/ Pa·s		35,240	≥20000	T0620
135℃ viscosity/ Pa·s		2.43	≤3	T0625
Elastic recovery/%		98.1	≥80	T0662
Segregation/ ℃		0.8	≤2.5	T0661
TFOT (163 °C, 5 h)	Mass loss/%	0.04	±0.5	T0609
	Penetration ratio/%	85.7	≥65	T0604
	Ductility/ (cm, 5℃)	24.9	≥15	T0605
Solubility/%		99.4	≥99	T0607
Flash point/°C		315	≥245	T0611

Table 3
Properties of the rejuvenating agents.

Items		Units	regenerant-I	regenerant-II	regenerant-III
60℃ viscosity		Pa·s	84	279	314
Flash point		°C	268	271	274
Saturates content		%	20.4	22.6	23.8
Aromatic content		%	65.9	52.7	53.4
TFOT (163 °C, 5 h)	Viscosity ratio	/	1.49	0.79	0.81
	Mass variation	%	1.27	0.47	0.42

Table 4
Properties of the aged asphalt with different aging time.

Items Sample	Penetration(0.1 mm)	Ductility (5 °C, cm)	Softing point (℃)	Viscosity (135 °C, Pa·s)
Asphalt(RAP materials)	35	2.6	64.8	3.70
Asphalt(RTFOT 5 h)	48	22.8	74.2	2.71
Asphalt(RTFOT 7 h)	43	13.6	67.3	3.06
Asphalt(RTFOT 9 h)	36	3.3	63.00	3.40
Asphalt(RTFOT 11 h)	32	1.2	58.60	4.20
Asphalt(RTFOT 13 h)	30	0	57.8	4.45

2.3. Preparation of the rejuvenated SBS modified asphalt samples

According to the previous research [26], the rejuvenated SBS modified asphalt samples were prepared as follows. Firstly, the aged SBS modified asphalt was heated to 140℃ and poured into a container. When the temperature was increased to 150℃, 4.0% of the regenerant-I, regenerant-II, and regenerant-III were added to the aged SBS modified asphalt, and the mixture was blended for about 60 min to ensure the rejuvenator disperse well in asphalt binders. At last, the rejuvenated SBS modified asphalt samples were obtained for the following testing.

2.4. Measurement and characterization

2.4.1. Gel permeation chromatography

Gel permeation chromatography (GPC) is the most effective method for characterizing the molecular weight and distribution of organic materials [27,28]. And the Waters 1515 gel chromatograph was used to detect in this test. Firstly, the sample was dissolved in the tetrahydrofuran solution with a concentration of 2% − 3%. After the sample was completely dissolved after 24 h, a portion of the mixed solution was injected into the sample bottle through a 0.45 mm filter. And then, 0.5 mL of the prepared solution was measured and injected into the gel permeation chromatograph machine. Meanwhile, the testing conditions were set, including that the flow rate was 1.0 mL/min and the test temperature was 25 °C.

2.4.2. Fluorescent microscope

The fluorescence microscopy (FM) test is the most visual mean of observing the SBS polymer dispersion in the modified asphalt system [29]. And SBS phase could apparent yellow fluorescence in the blue region due to its unique structure, resulting in the SBS phase and asphalt phase in the SBS modified asphalt system being distinguished in the fluorescence microscope, which can clearly and intuitively observe the change of two-phase structure. In this section, the morphology of the SBS modified asphalt samples before and after aging, and the rejuvenated SBS modified asphalt samples were characterized according to the previous method suggested by Dong et al., [30].

2.4.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) can be used to investigate the thermal behavior of the SBS modified asphalt and evaluate the high and low-temperature performance of asphalt binders [31]. In this section, the glass transition temperature and the total heat absorption peak energy of the samples were selected to assess the regeneration effect of aged SBS modified asphalt. During the detection process, the experimental temperatures ranged from −80 °C to 240 °C, the nitrogen flow rate was at 50 mL/min, and the temperature increase rate was 10 °C/min.

2.4.4. Conventional properties tests

The conventional properties of SBS modified asphalt samples, including the softening point, the ductility at 5℃, the penetration at 25 ℃, viscosity, and storage stability, were determined according to T0606, T0605, T0604, and T0625 methods in JTG E20-2011-Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering, which is belongs to the China Industry Standards.

2.4.5. Contact angle test and adhesion analysis

Recently, there have been few studies focused on the change of adhesion for aged asphalt binders before and after regeneration, which has a significant effect on the water damage of recycled asphalt mixture. And the surface free energy from the contact angle tests is an effective index to evaluate the adhesion of materials [32]. Therefore, the surface free energy and adhesion of the samples before and after aging and regeneration were calculated and analyzed by the contact angle experiments. During the experiments, the testing liquids, including distilled water, glycerol, and formamide, were selected, and the surface energy parameters of the three liquids and the basalt aggregate are listed in Table 5 and Table 6. The surface energy and parameters of samples were combined with equation ①, and the adhesion of the samples was calculated by the equation ②. Meanwhile, the ambient temperature of the experiment was 25 °C.

$$\frac{(1+\cos\theta)}{2}\frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\times\sqrt{\frac{\gamma_l^p}{\gamma_l^d}}+\sqrt{\gamma_s^d} \quad (1)$$

$$W_a = 2\sqrt{\gamma_s^d\gamma_l^d}+2\sqrt{\gamma_s^p\gamma_l^p} \quad (2)$$

where θ in the formula is the contact angle, γ_l is the liquid surface free energy, γ_l^d is the liquid dispersive surface energy component, γ_l^p is the liquid polar surface energy component, γ_s^p is the polar surface energy component of the test sample, γ_s^d is the dispersive surface component of the test sample, and W_a is the work of adhesion.

3. Results and discussion

3.1. Molecular structure

The GPC curves of SBS modified asphalt, including original, aged, and rejuvenated samples, are drawn in Fig. 3. It can be seen that the prominent peaks are in the range of retention time from 15 min to 20 min, reflecting the molecular weight distribution characteristics of the asphalt [33]. And there is a small peak in the range of 13 min to 15 min on the left of the curves, which is the distribution of the high molecular weight of the SBS modifier [34]. Meanwhile, the prominent characteristic peaks of all asphalt samples centralize around 18.51 min. Compared to the original SBS modified asphalt, the prominent peak of the aged SBS modified asphalt has a slight leftward shift to 18.23 min, indicating that the molecular weight of the asphalt binder begins to increase, which results from there is some oxidation reaction in the asphalt binder during the aging process or the service life, and amounts of components polymerize from the low molecular weight to high molecular weight [35]. While the regenerant-I and regenerant-II were added to the aged SBS modified asphalt samples, the molecular weight distribution of the asphalt binders has been improved to be similar to the original asphalt,

Table 5
Surface energy index of experimental liquids.

Liquid name	Surface free energy (mJ/m^2)		
	γ_l	γ_l^d	γ_l^p
Distilled water	72.8	21.8	51.2
Formamide	58.1	39.5	18.6
Glycerol	63.5	26.6	36.9

Table 6
Surface energy index of tested materials.

Material	Surface free energy(mJ/m^2)		
	γ_l	γ_l^d	γ_l^p
Basalt	52.38	35.5	16.88

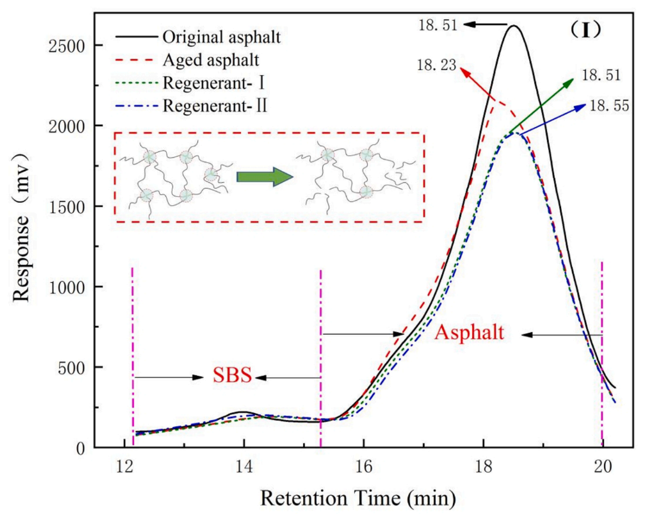

Fig. 3. The GPC curves of all asphalt samples.

which could balance the colloidal structure in the aged asphalt due to a large number of light components in the rejuvenators.

To understand the change of molecular weight of the SBS modifier, the GPC curve for retention times of 12–15 min was amplified in Fig. 3 (II). Among them, the small peak of the original SBS modified asphalt appears at 13.96. In contrast that of the aged SBS modified asphalt shows a rightward shift to 14.48 min, indicating a reduction in the molecular weight of SBS after aging. This is mainly due to unsaturated bonds in the polybutadiene segment of the SBS modifier, which is prone to react during the thermal-oxidative aging process. Moreover, the hydrogen on the carbon atoms adjacent to the double bonds is prone to oxygen absorption and oxidation, which accelerates the oxidative degradation of SBS [25]. However, there were different changes in the molecular weight distribution in the range of 12 min-15 min, when the regenerant-I and regenerant-II were added to the aged SBS modified asphalt. As for the regenerant-I, the small peak continues to rightward shift to 14.56 min, which can be seen that the regenerant-I cannot restore the molecular weight of the SBS modifier in the aged asphalt binder. It is fortunately found that adding the regenerant-II has a significant leftward shift to 14.26 min, indicating that the regenerant-II has the ability to supplement the degraded SBS in the aged modified asphalt to a certain extent.

Furthermore, the average molecular weights, including Mn and Mw, were analyzed in Fig. 4. When the SBS modified asphalt was aged, the values of Mn and Mw decreased to 1145 and 6903; that is to say, the degradation of SBS polymer dominates the aging of SBS modified asphalt. And it is easy to understand why the values of Mn and Mw continued to decrease when the regenerant-I with high aromatics content is added. However, adding the regenerant-II could increase the values of Mn and Mw of SBS modified asphalt because the regenerant-II can supplement the SBS modifier and reform the cross-linking structure, which is consistent with the results of changes in the molecular weight distribution. And the flows of the thermal oxygen degradation reaction and the regeneration effect of regenerant-II in the aged SBS modified asphalt are shown in Fig. 5.

3.2. Morphology

The morphology of the SBS modified asphalt, including original, aged, and rejuvenated samples by fluorescence microscopy test, is presented in Fig. 6. It can be clearly seen that the SBS phase is uniformly dispersed in the original SBS modified asphalt, and the SBS particle size is small (Fig. 6(a)). Overall, the whole structure of the system is very dense. However, when the SBS modified asphalt is aged, massive agglomeration of the SBS modifier in asphalt happen, and the network structure is severely damaged (Fig. 6(b)). The reason is that when the SBS modified asphalt is stored at a high temperature, the SBS modifier will generate some fragments with hydroxyl and carboxyl polar groups, which are easy to agglomerate. This is because the SBS modifier will generate some fragments with hydroxyl and carboxyl polar groups under high temperatures, and these polar fragments [36].

In order to restore the morphology of the aged SBS modified asphalt, the regenerant-I with a high aromatic component was used to rejuvenate, as shown in Fig. 6(c). It can be found that although a few large SBS phase particle is still present in the SBS modified asphalt, most agglomerated particles have been dispersed, and the SBS modifier is loosely distributed in density. In a word, compared to aged SBS modified asphalt, the regenerant-I with a high aromatic component has improved the SBS modifier aggregation to some extent. And the polymer solution theory and solubility parameter theory can explain the above phenomenon. It can be assumed that the system consists of two components, including that the solute is SBS modifier and the solvent is the rejuvenate agent. Whether the solvent and solute can form a stable solution depends

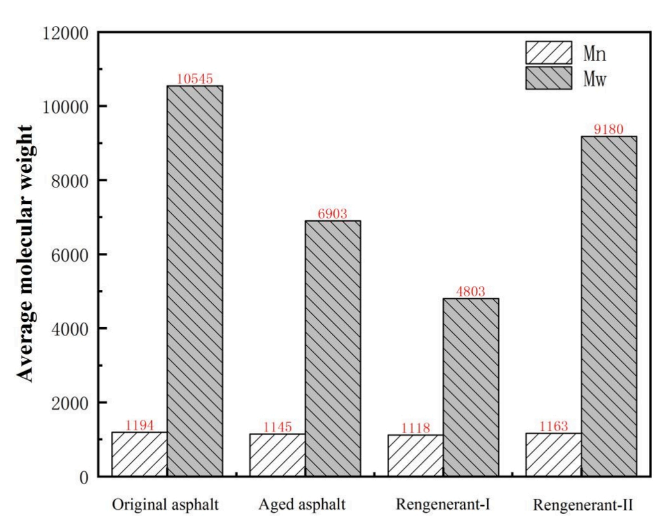

Fig. 4. The average molecular weight of all asphalt samples.

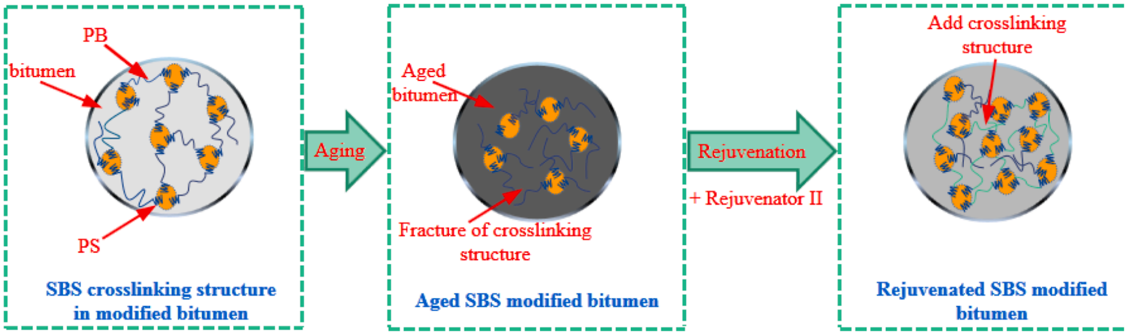

Fig. 5. Aging degradation and rejuvenation of SBS modified asphalt in molecular structure.

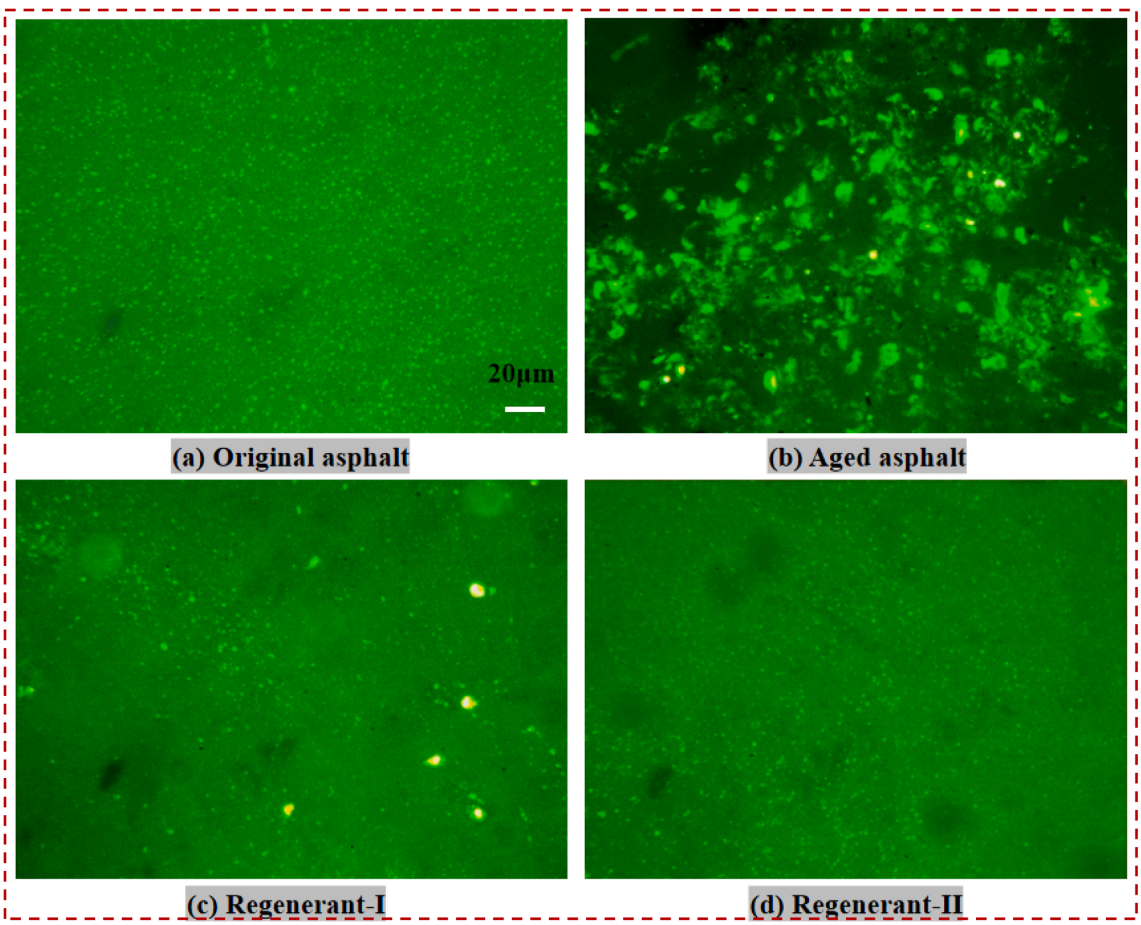

Fig. 6. Morphology of all modified asphalt samples (a) Original SBS modified asphalt, (b) Aged SBS modified asphalt, (c) Rejuvenated SBS modified asphalt with Regenerant-I, and (d) Rejuvenated SBS modified asphalt with Regenerant-II.

on the compatibility of the two components, which is the solubility of the solvent to the solute. And when the solubility of the substances is similar, a stable solution could be formed. Furthermore, it is known that the solubility parameter of the SBS modifier is 8 to 10 (4.186 8 J/cm^3) [37], while the solubility of aromatic substances is around 9.15 (4.186 8 J/cm^3). Therefore, the rejuvenator with high aromatics content can effectively disperse the agglomerated SBS modifier and enhance the performance of the aged modified asphalt to a certain extent. More obviously, the regeneration effect of the aged SBS modified asphalt is best when the regenerant-II is added. The agglomerated particles disappeared, and the SBS modifier was dispersed uniformly in the system, similar to that of the original SBS modified asphalt. Compared to the regenerant-I, the regenerant-II can not only spread the agglomerated SBS, but also replenish a part of the SBS polymer that degradation during the aging process, and reform the cross-linking structure due to the regenerant-II is consisted of SBS polymer and the cross-linking agent.

3.3. Phase transition and thermal behavior

The thermal behavior of SBS modified asphalt, including original, aged, and rejuvenated samples, were evaluated by the DSC tests. And the change in aggregation state can be analyzed by the absorption peak position and heat absorption from the DSC spectrum. In general, the higher the endothermic peak is, the more the changes in the number of components are. Meanwhile, the wider the peak is, the more types of components change and the more unstable the system is [38]. And then, the DSC curves are drawn in Fig. 7, and the absorbed heat of all modified asphalt samples is analyzed in Table 7.

The glass transition temperature (T_g) can be used to evaluate the low-temperature performance of modified asphalt. And the values of T_g of SBS modified asphalt, including original, aged, regenerant-I, and regenerant-II, are presented in Fig. 7, which are −16.324℃, −3.741℃, −7.493℃, and −11.24℃, respectively. Compared to the original SBS modified asphalt, the T_g of aged SBS modified asphalt has a significant increase from −16.324℃ to −3.741℃, indicating that the aging process has a harmful effect on the low-temperature performance. That is because the fact that the light components of SBS modified asphalt have been volatilized to a certain extent and transferred to asphaltenes during the high-temperature therm-oxidative aging and service life period, and the SBS molecules and cross-linking structure are degraded [39]. While the T_g values of regenerant-I and regenerant-II samples decrease to −7.493℃ and −11.24℃ compared with aged SBS modified asphalt. It can be seen that adding rejuvenator could improve the low-temperature performance of aged SBS modified asphalt. Meanwhile, there are different changes in the low-temperature performance of regenerant-I and regenerant-II. Among them, the regenerant-I can only recover the low-temperature performance of the aged bitumen to a small extent by adjusting the four components of the asphalt. While the regenerant-II not only restores the components but also effectively supplements the degraded SBS polymer and broken cross-linking structure, thereby significantly improving the low-temperature performance of the aged SBS modified asphalt. In a word, the regeneration performance of regenerant-II is better than that of regenerant-I, consistent with the results from the previous GPC and fluorescence microscopy experiments.

Moreover, the thermal behavior of SBS modified asphalt shows the different changes in the process of aging and regeneration. And the total endothermic peak energy of SBS modified asphalt, including original, aged, regenerant-I, and regenerant-II, are 2.173 J/g, 3.861 J/g, 3.228 J/g, and 2.432 J/g, respectively. The smaller the value of endothermic peak energy is, the more unstable the performance of asphalt is [40]. And the aging process makes increase the endothermic energy, while adding rejuvenator could decrease the endothermic energy and improves the performance of modified asphalt. Compared with regenerant-I, the value of endothermic energy of regenerant-II is closer to that of original SBS modified asphalt. It can be indicated that the regenerant-II has a better regeneration effect on SBS modified asphalt, and a part of the damaged SBS network structure can be reconstructed, which promotes the overall performance of the rejuvenated asphalt more stable.

3.4. Macro conventional performance

The conventional performance of SBS modified asphalt including original, aged, regenerant-I, and regenerant-II are presented in Fig. 8. It can be found that the softening point, penetration, and ductility of SBS modified asphalt decreased. Meanwhile, the viscosity increased after the aging process, which indicates that the aging process promotes the light components to decrease and asphaltenes content to increase, leading to the hardening and brittleness for SBS modified asphalt. When the regenerant-I with high range of aromatics was added to the aged SBS modified asphalt, the softening point and viscosity showed a decrease, and the viscosity decreased to 2.15 Pa·s, which is lower than that of the original SBS modified asphalt. Meanwhile, the ductility and penetration increased significantly, indicating that the light component in the rejuvenator can effectively improve the low-temperature performance of the aged asphalt, while greatly reducing the high-temperature performance. The above phenomenon is attributed to the diffusion behavior

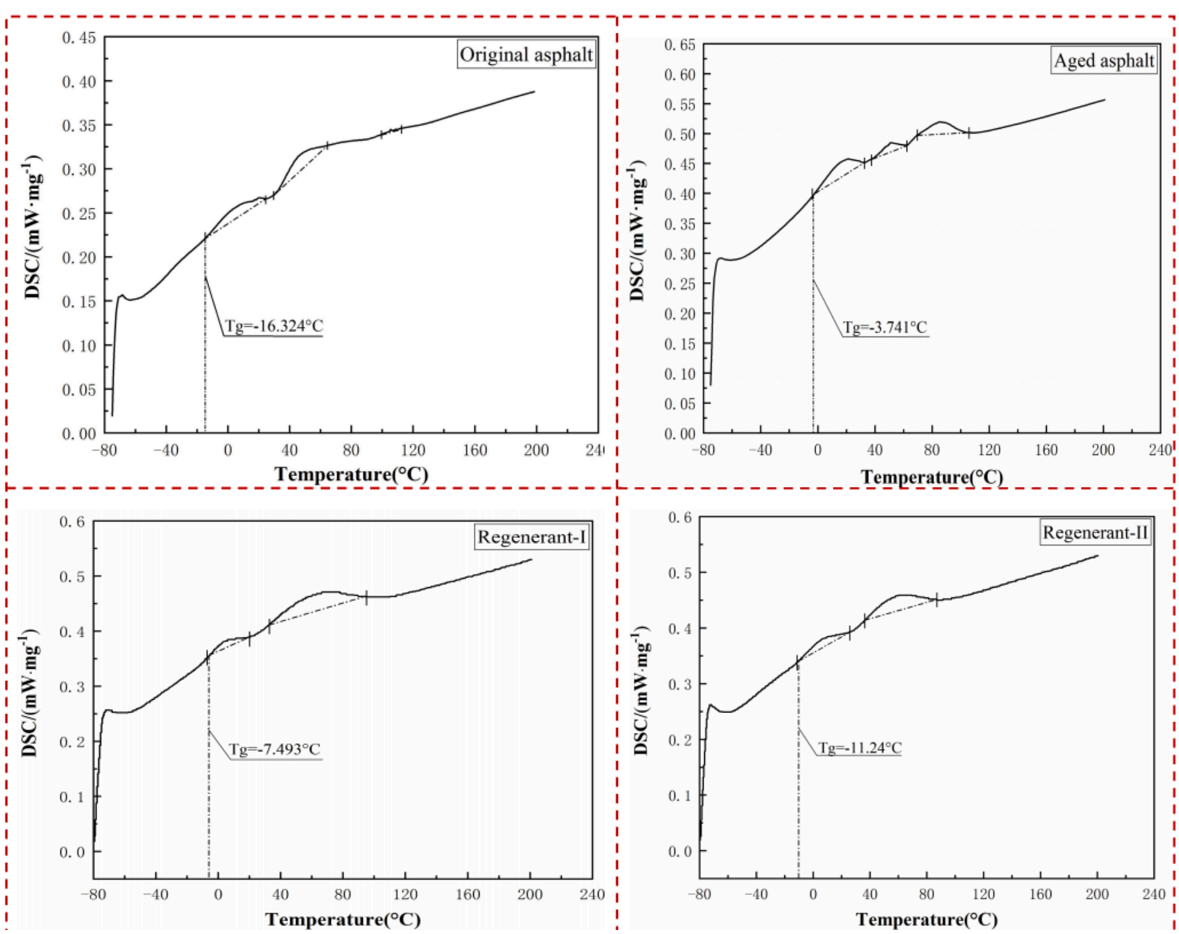

Fig. 7. DSC curves of all modified asphalt samples.

Table 7
Absorbed heat of all modified asphalt samples.

Sample	T_g/°C	Temperature interval		Heat absorption peak energy/(J/g)	Total heat absorption peak energy/(J/g)
		Peak temperature/°C	peak width /°C		
Original asphalt	−16.324	19.725	−21.402 ~ 24.67	1.098	2.173
		51.044	32.688 ~ 65.055	0.788	
		105.44	98.022 ~ 110.385	0.287	
Aged asphalt	−3.741	21.374	−1.7 ~ 32.912	1.353	3.861
		51.044	39.505 ~ 62.582	0.915	
		86.484	68.824 ~ 108.736	1.593	
Regenerant-I	−7.493	8.054	−12.667 ~ 20.465	1.121	3.228
		71.779	38.847 ~ 100.698	2.107	
Regenerant-II	−11.240	13.027	−17.637 ~ 20.465	1.011	2.432
		66.009	37.847 ~ 91.297	1.421	

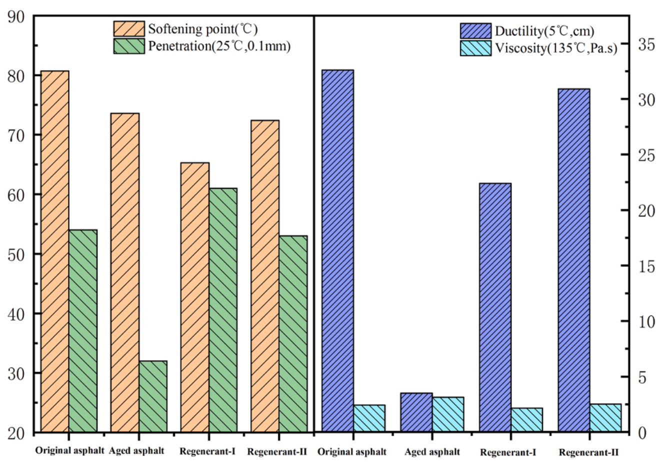

Fig. 8. The conventional performance of all modified asphalt samples.

of aromatic oil of regeneration agent in aged asphalt. And the diffusion mechanism can be explained by the 'molecular diffusion theory'. That is, the mutual diffusion process at the molecular level is the thermal movement from the high concentration area to the low concentration area, and when there is no concentration gradient, the mutual diffusion process will stop. Therefore, when the aromatic component from the regeneration agent diffuses uniformly in aged asphalt, the whole components will be reconciled, and the proportion of light components will increase, which will have a negative effect on the high-temperature performance of aged SBS modified asphalt.

Furthermore, when the regenerant-II was added to the aged SBS modified asphalt, the softening point and ductility were increased to 72.4℃ and 30.9 cm, which were recovered by 89.7% and 94.8% of original SBS modified asphalt. Therefore, the self-made regenerant-II could improve the high and low performance of aged SBS modified asphalt, due to the SBS polymer in the rejuvenator playing a complementary role in reforming the SBS network structure. In addition, the change in the conventional performance of SBS modified asphalt can be explained by the above results from the microstructure experiments.

3.5. Interface adhesion characteristics

The researchers pointed out that the rejuvenator could restore the conventional performance of aged SBS modified asphalt, such as softening point, ductility, and penetration [41]. However, the adhesion of regenerated asphalt, which is an essential index for the water stability of regenerated asphalt mixture, has been rarely studied. Therefore, the regenerant-III with the interfacial reinforcing agent was prepared to investigate the improvement of adhesion for regenerated asphalt. And the contact angle test was used to characterize the effect of different rejuvenators on the adhesion, as presented in Table 8, and the values of surface energy and adhesion work were analyzed in Fig. 9 and Fig. 10.

Table 8
The contact angle of all modified asphalt samples.

Samples	Distilled water	Glycerol	Formamide
Original asphalt	96.43	89.24	77.94
Aged asphalt	102.3	94.30	83.3
Regenerant-I	100.26	93.26	81.96
Regenerant-II	98.37	91.37	80.17
Regenerant-III	96.63	89.44	78.89

It can be seen that the contact angels of the samples with original, aged, and different rejuvenators shows different changes, and the descending orders of the contact angels are aged asphalt, regenerant-I, regenerant-II, regenerant-III, and original asphalt. And the aging process promotes to increase significantly the contact angle of SBS modified asphalt due to the thermal degradation of SBS polymer and the increase of asphaltenes content, which has excellent benefits to increasing the hydrophobicity of asphalt binder [42]. Nevertheless, the addition of regenerant-II can better solve the above problems by increasing the light components, supplying the SBS polymer, and reforming the network structure. Meanwhile, the interfacial reinforcing agent presented in the regenerant-III could improve the interface characteristics for the aged SBS modified asphalt better than that of regenerant-II. And above results can be explained why the regenerant-I has a limited regeneration effect for aged SBS modified asphalt.

The surface energy, polar component, and dispersion component of SBS modified asphalt, including original, aged, regenerant-I, regenerant-II, and regenerant-III were calculated by the equation ①, as shown in Fig. 9. It can be found that the surface energy of aged SBS modified

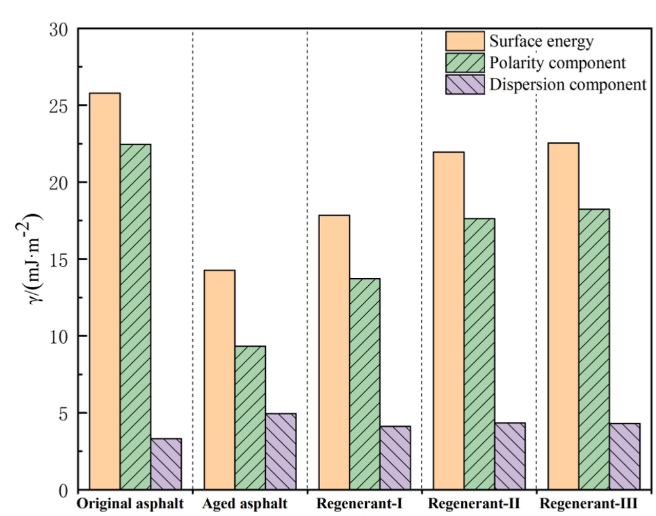

Fig. 9. Surface energy and its components of all modified asphalt samples.

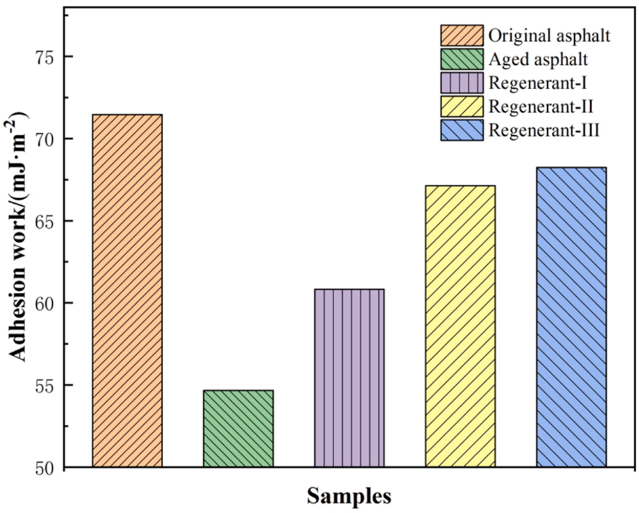

Fig. 10. Adhesion work of all modified asphalt samples.

asphalt decreased by 44.67% compared to the original SBS modified asphalt, and the polar component increased and the dispersion component decreased. One reason is that the light components such as saturates and aromatics were volatilized during the aging process, and another is that the chemical reaction happened to convert the light components to asphaltenes. Among them, the saturates and aromatics in asphalt are non-polar components, while the asphaltenes are polar components [43]. Meanwhile, the different rejuvenators have different effects on the surface energy, dispersion components, and the polar components of aged SBS modified asphalt. When the regenerant-I was added, the dispersion component increased, and the polar component decreased, due to the supplement of light components. While the regenerant-II not only can improve the dispersion component but also reform the network structure, which slightly increases the viscosity of the rejuvenated modified asphalt and then increases the polar component. And above results are consistent with the previous conventional performance. Furthermore, the regenerant-III has a slight effect on the surface energy, polar component, and dispersion component of aged SBS modified asphalt compared with the regenerant-II.

As an important indicator for evaluating adhesion between asphalt and aggregate, the adhesion work of all samples was calculated by the equation ②, presented in Fig. 10. The adhesion work of original SBS modified asphalt is 71.463 mJ/m^2, while the aging process decreases the adhesion work by 23.51%. It can be concluded that the aging process hurts the adhesion between asphalt and aggregate, and it is necessary to explore an effective method to improve the adhesion property. Meanwhile, there is significant variance in the adhesion of regenerated asphalt prepared by different rejuvenator. When regenerant-I was added to aged SBS modified asphalt, the adhesion work increased by 11.29%, while the adhesion work increased to 22.83% as regenerant-II was added. As for the regenerant-III, the adhesion work was restored to 95.49% of the original SBS modified asphalt due to the action of the interfacial reinforcing agent. Han et al., [44] prepared one kind of rejuvenator (HHA) and found that it can restore the surface energy of aged SBS modified asphalt to 82.33% of the virgin sample, which is lower than that of The regenerant-III. And the mechanism of regenerant-III on the interface between asphalt and basalt is drawn in Fig. 11. The main reason is that the hydroxyl functional groups in the interfacial reinforcing agent can react with the hydroxyl groups of basalt to form

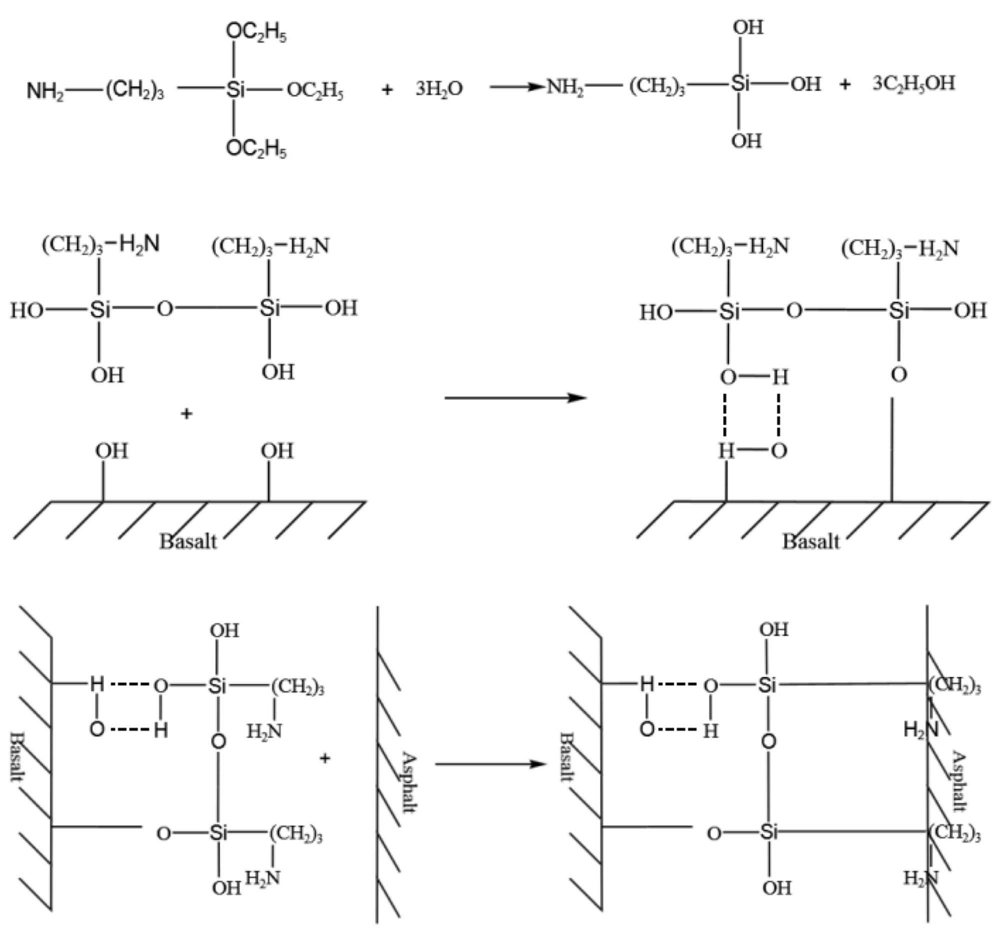

Fig. 11. Mechanism of regenerant-III on the interface between basalt and asphalt.

hydrogen bonds, which are then converted into covalent bonds through hydrolysis, condensation, and dehydration. Meanwhile, the methylene group and amino group at the other end of the interfacial reinforcing agent could combine with the asphalt binder to form a strong interfacial bond, thereby enhancing the adhesion between asphalt and aggregate.

4. Conclusion

To comprehensively improve the performance of recycled SBS modified asphalt mixture, the highly efficient and environmentally friendly rejuvenator with waste thermal conductive oil, polymer, and the interfacial reinforcing agent was prepared in this paper. And the influence of the different rejuvenators on the rejuvenation mechanisms of aged SBS modified asphalt was characterized by different scales, which included the molecule structure, morphology, phase transition and interface adhesion characteristic, and macro performance investigated by means of GPC tests, FM tests, DSC tests, contact angle tests, and conventional performance tests, respectively. And the conclusions can be drawn as follows.

(1) The thermal-oxidative aging process leads to an increase in the molecular weight of the asphalt binder, while a reduction in the weight of the SBS modifier is due to the degradation. The regenerant-I and regenerant-II could improve the molecular weight distribution of asphalt binders. What's more, the regenerant-II also can supplement the SBS modifier and reform the cross-linking structure of aged SBS modified asphalt.

(2) The massive agglomeration of the SBS phase happened in the aged SBS modified asphalt. The rejuvenator with high aromatics content can effectively disperse the agglomerated SBS modifier and enhance the performance of the aged modified asphalt to a certain extent. The regenerant-II has a better recovery effect on the morphology structure of aged SBS modified asphalt than that of the regenerant-I.

(3) The Tg and endothermic energy of SBS modified asphalt increased after the aging process, which has negative effect on the low-temperature performance and thermal stability. The regenerant-II can resume the thermal behavior of aged SBS modified asphalt better than that of the regenerant-I.

(4) When SBS modified asphalt was aged, the softening point, penetration, and ductility decreased, while the viscosity increased. The addition of regenerant-I has more significant damage to the softening point of aged SBS modified asphalt. The regenerant-II could recover the softening point and ductility by 89.7% and 94.8% of the original SBS modified asphalt.

(5) The adhesion work of SBS modified asphalt decreased by 23.51% after the aging process. The adhesion of aged SBS modified asphalt had significantly changes when the rejuvenators with different components were added. Under the action of the interfacial reinforcing agent, the regenerant-III could improve the adhesion work to 95.49% of the original SBS modified asphalt.

CRediT authorship contribution statement

Fuqiang Dong: Conceptualization, Funding acquisition, Methodology, Writing – original draft. **Jincheng Wang:** Methodology, Writing – original draft. **Xin Yu:** Resources. **Mengmeng Jiang:** Investigation. **Yongjia Guo:** Resources, Validation. **Shiyu Wang:** Formal analysis. **Yuanzhe Zu:** Data curation. **Shisong Ren:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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