

Research Article

Effect of Recycling Agents on Rheological and Micromechanical Properties of SBS-Modified Asphalt Binders

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Individual effect of aging and rejuvenator recycling on basic properties of asphalt is readily recognized, but there is only limited understanding about whether the recycling of SBS- (styrene-butadiene-styrene-) modified asphalt is an inverse process of aging or not. To compare the effects of aging and rejuvenator on microproperties and molecular composition of SBS-modified asphalt, comprehensive performance tests and physical-chemistry experiments were conducted. The results of infrared spectroscopy tests demonstrate that the reticular crosslinking structure of asphalt was destroyed and SBS's modification effect was gradually lost after aging. This can cause the strengthening of high-temperature performance and reduction of the low-temperature anticrack property of SBS-modified asphalt. Scanning electron microscope shows that the island structure of SBS-modified asphalt disappeared after aging. Energy spectrum analysis shows that the C (carbon) content of aged SBS-modified asphalt has decreased, while the O (oxygen) content and S (sulfur) content have increased obviously. Results of the fluorescence microscope, SEM, and rheological tests show that the epoxy functional group compounds of aliphatic glycidyl ether resin had high reactivity; the triblock molecular structure of SBS and the mechanical performance of SBS-modified asphalt were recovered.

1. Introduction

Traffic flow has been growing with the rapid development of China's highway construction, and many of the asphalt pavements built early in China have been damaged under heavy traffic pressure. Many high-grade road highways have approached or entered their maintenance period according to their design life and actual use conditions. It is estimated that, from now on, about 12% of asphalt pavement will need overhauling every year. At the same time, faced with the resourceful provinces' rising demand for transport capacity of the high-grade highway, China has been carrying out the reconstruction and widening project of the high-grade

highways in recent years. Both the overhaul and medium maintenance and reconstruction and widening of asphalt pavement produce a lot of reclaimed asphalt pavement (RAP). According to statistics, more than 35 million cubic meters of RAP are produced in overhaul and medium maintenance and widening of highways in China, and the figure grows at a rate of 15% per year and will reach 100 million cubic meters in ten years. The stacking, discarding, and degradation of such a huge amount of waste materials will aggravate the increasing serious environment pressure and resource problems. Therefore, using the RAP more efficiently is one big challenge in the field of highway construction.

Researchers have done a lot of research works, respectively, in the aspects of the physical properties decay law, component change law, and molecular structure changes. However, these were mainly done through indoor aging tests, and many factors affecting asphalt aging remain to be studied further, such as influence mechanism of water on asphalt aging, the relationship, and the difference between simulated and natural aging. Therefore, we also need to further study the asphalt aging performance and mechanism using advanced modern analytical test methods and various aging test methods to provide a theoretical basis for asphalt pavement recycling [1–7]. Zhang et al. studied the three types of aging methods on the performance of SBS- (styrene-butadiene-styrene-) modified asphalt, including thin film oven test (TFOT), pressure aging vessel (PAV), and ultraviolet (UV) radiation. They found that SBS-modified asphalt with penetration 90 had a higher retained penetration and ductility as well as the lower viscosity aging index compared to SBS-modified asphalt with penetration 70 [8].

At present, no definitive conclusion has been drawn from the mechanism of interaction between the recycling agent, aged asphalt, and new asphalt. For example, the measured data of some recycling projects show that the stiffness of recycled asphalt pavement is lower than the designed value. One explanation for this phenomenon is that the recycling agent fails to diffuse into the reclaimed asphalt. Therefore, it is of great significance for the asphalt recycling technology to study the law of recycling agent's diffusion into asphalt and recycling agent's peptization effect on asphalt and reveal the microproperties of recycling asphalt [9–15]. Xiao et al. studied the low-temperature performance characteristics of RAP mortars containing sieved RAP and soft binders at three aged states; they found that RAP mortar with a higher old binder content had a higher minimum low temperature regardless of the RAP source [16]. RAP mortars with virgin soft binder had the best low-temperature resistance followed by the RAP mortars with RTFO and PAV binders. However, it is still in doubt whether SBS-modified asphalt is recyclable. Supporters believe that SBS-modified asphalt is produced only by physical modification of base asphalt, while asphalt recycling involves more chemical reactions than a physical reaction. Therefore, SBS-modified asphalt recycling is only the recycling of aged asphalt and does not have effect on the SBS copolymer [17, 18]. Opponents believe that the aging process of SBS-modified asphalt includes the aging of both asphalt and SBS copolymer. Therefore, the recycling of SBS-modified asphalt inevitably includes the recycling of the SBS copolymer. To this end, recycling agents developed by researchers have different application scopes, and it is unknown whether they can be used for SBS-modified asphalt recycling [19–23]. In view that SBS-modified asphalt is adopted for surface and middle courses of most high-grade highways in China, it is of great practical significance to find a recycling agent applicable to SBS-modified asphalt.

The objective of this study was to investigate the mechanisms of aging and recycling of SBS-modified asphalt by conducting comprehensive performance tests and

physical-chemistry experiments and further to demonstrate whether the two processes were an inverse or not.

2. Materials and Methods

2.1. Materials. SBS-modified asphalt was used in this research. Two typical rejuvenators were selected to recover the aged asphalt binder in this research. The molecular structural formulas of rejuvenator A and rejuvenator B and the curing agents used in this research are shown in Figure 1.

2.2. Laboratory Tests. In this research, both conventional and advanced tests have been conducted. The conventional tests are used to evaluate the effect of the aging-recycling cycle on rheology of SBS-modified asphalt at the macrolevel. The advanced tests are used to investigate the mechanism of effect of the aging-recycling cycle on rheology of SBS-modified asphalt at the microlevel.

2.2.1. Penetration. Penetration is a widely used method in the world to measure asphalt stiffness. The smaller the stiffness, the greater the penetration would be. The greater the stiffness, the smaller the penetration would be. It is sure that stiffness change can reflect not only the asphalt aging but also the effect of SBS modification. Three replicates were tested in this research, and the data shown in this paper were the average of the three replicates.

2.2.2. Softening Point. The softening point is the temperature at which a material softens beyond some arbitrary softness. A ring and ball apparatus can also be used for the determination of the softening point of bituminous materials. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

2.2.3. Ductility. Ductility is a solid material's ability to deform under tensile stress. The ductility of the bituminous material is defined as the distance in centimeters, to which it will elongate before breaking when two ends of a briquet specimen of the material are pulled apart at a specified speed and a specified temperature. Three replicates were tested in this research, and the data shown in this paper were the average of the three replicates.

2.2.4. Viscosity. The rotational viscometer was used to measure binder viscosity at 135°C. First, a sample was placed in a chamber that was heated to the test temperature. Second, the sample viscosity was measured by rotating the spindle immersed in the binder. The rotational speed was set at 20 revolutions per minute (RPM), and the viscosity reading was recorded in units of centipoise. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

2.2.5. Gel Permeation Chromatography (GPC). Gel permeation chromatography (GPC) has low requirements for flow

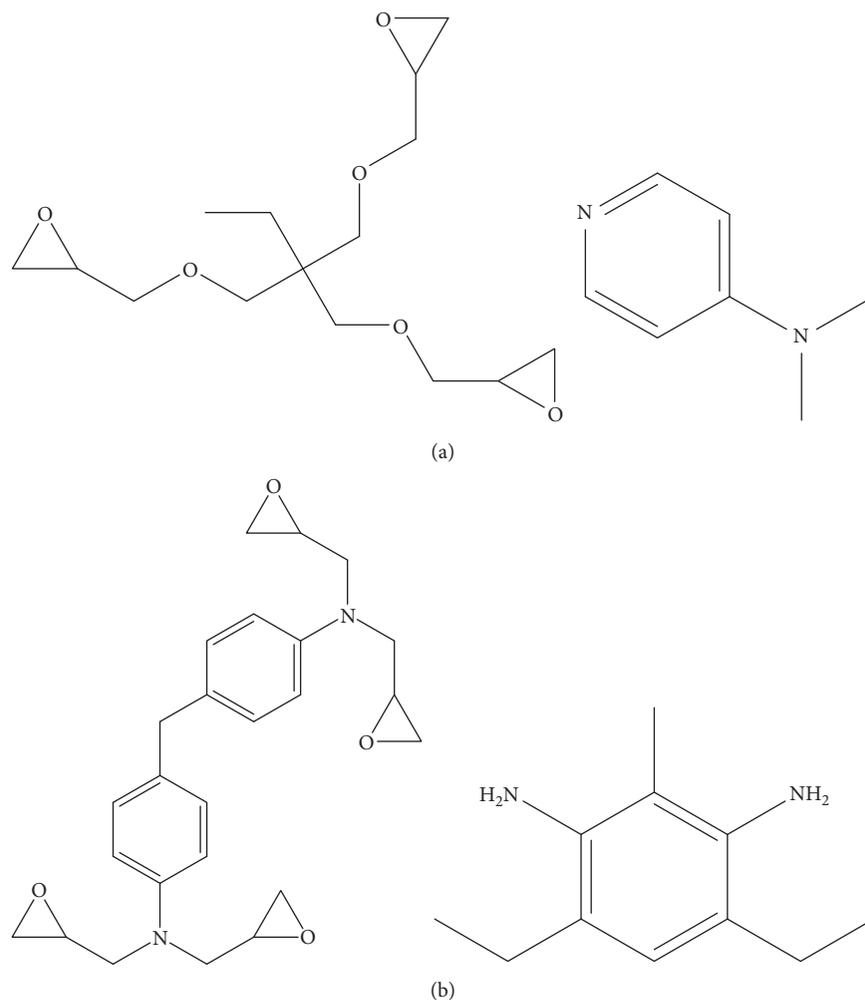


FIGURE 1: Molecular structural formulas of rejuvenators and the curing agents. (a) Rejuvenator A: fat glycidyl ether epoxy resin (left) and its curing agent (right). (b) Rejuvenator B: glycidyl amine epoxy resin (left) and its curing agent (right).

phase and features moderate test conditions, good repeatability, and fast analysis speed. It is currently the most widely used method for determining the molecular weight distribution of high polymer materials. Its separation basis is different hydrodynamic volumes of solute molecules in solution. The molecular elution volume of the solute depends on the physical parameters such as molecular dimension, filler aperture, porosity, and column volume. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

2.2.6. Thermogravimetric Analysis (TGA). To further reveal the changes before and after SBS-modified asphalt aging, the thermogravimetric (TG) test was conducted on SBS-modified asphalt and aged SBS-modified asphalt to analyze the thermal gravimetric property. Q600SDT TGA produced by TA Instruments was adopted for the TG test, with a temperature range of room temperature to 1500°C, a sensitivity of 0.1 μ g, and a temperature accuracy higher than 2%. The test was conducted in a nitrogen atmosphere at a temperature rise rate of 10°C/min and at a temperature range from room

temperature to 1,000°C. Samples were made with SBS-modified asphalt before and after aging, respectively, and put in TGA for comprehensive thermal gravimetric analysis. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

2.2.7. Hydrogen Nuclear Magnetic Resonance (1HNMR) Spectrometry. Hydrogen nuclear magnetic resonance (1HNMR) spectrometry is conducted with Bruker AV-400 MHz NMR, with CDCl₃ as the solvent, TMS as the internal reference, and a test temperature of 25°C. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

2.2.8. Scanning Electron Microscope (SEM). Scanning electron microscope (SEM) is a method observing micro properties. It can be directly used for microimaging of the matter properties of the sample surface material. In principle, SEM scans the sample with a very thinly focused high-energy electron beam to stimulate various physical

information, which is received, amplified, and imaged to get the observation results of the sample surface.

2.2.9. Energy Dispersive Spectrometer (EDS). Energy dispersive spectrometer is used for analyzing the types and content of microarea elements of the material, which is used together with an electronic microscope and transmission electron microscope. Different elements have their own characteristic wavelengths of X-ray, which depend on the characteristic energy ΔE released during energy transition. Energy spectrometer conducts composition analysis according to different characteristic energies of X-ray photons of different elements.

When X-ray photons enter the detector, they will stimulate a certain number of electron-hole pairs in the Si (Li) crystal. The minimum average energy ϵ for producing an electron-hole pair is constant (3.8 eV at low temperature), and the number of electron-hole pairs produced by one X-ray photon is $N = \Delta E/\epsilon$. Therefore, the greater energy the incident X-ray photons have, the bigger the N will be. Biases installed on both ends of the crystal are used to collect electron-hole pairs, which are converted to current pulses by the preamplifier. The height of current pulses depends on the size of N . Current pulses are then converted into voltage pulses by the main amplifier and enter the multichannel pulse height analyzer, which classified and counted the pulses by height. Thus, a diagram of X-ray distribution according to energy is obtained. Two replicates were tested in this research, and the data shown in this paper were the average of the two replicates.

3. Results and Discussion

3.1. Aging of SBS-Modified Asphalt. In order to find the role of SBS-modified asphalt aging, the laboratory adopted I-D modified asphalt meeting the requirements of Technical Specification for Construction of Highway Asphalt Pavements (JTG E20-2011) as a sample and put it in an RTFOT at 163°C for aging for 16h and then put the asphalt aged by RTFOT in a PAV at 100°C for aging for 20h. Finally, the changes in performance indicators, functional groups, components, and molecular weight of the aged SBS-modified asphalt were analyzed.

3.1.1. Effects of Aging on the Thermodynamic Performance of SBS-Modified Asphalt. Figure 2 presents TG curves before and after SBS-modified asphalt aging. This figure shows that the thermal weight loss of SBS-modified asphalt in a nitrogen atmosphere had one phase. Little residue carbon is left at 540°C, and combustion is completed. The thermogravimetric processes are consistent before and after SBS-modified asphalt aging, indicating that the aging effect is weak.

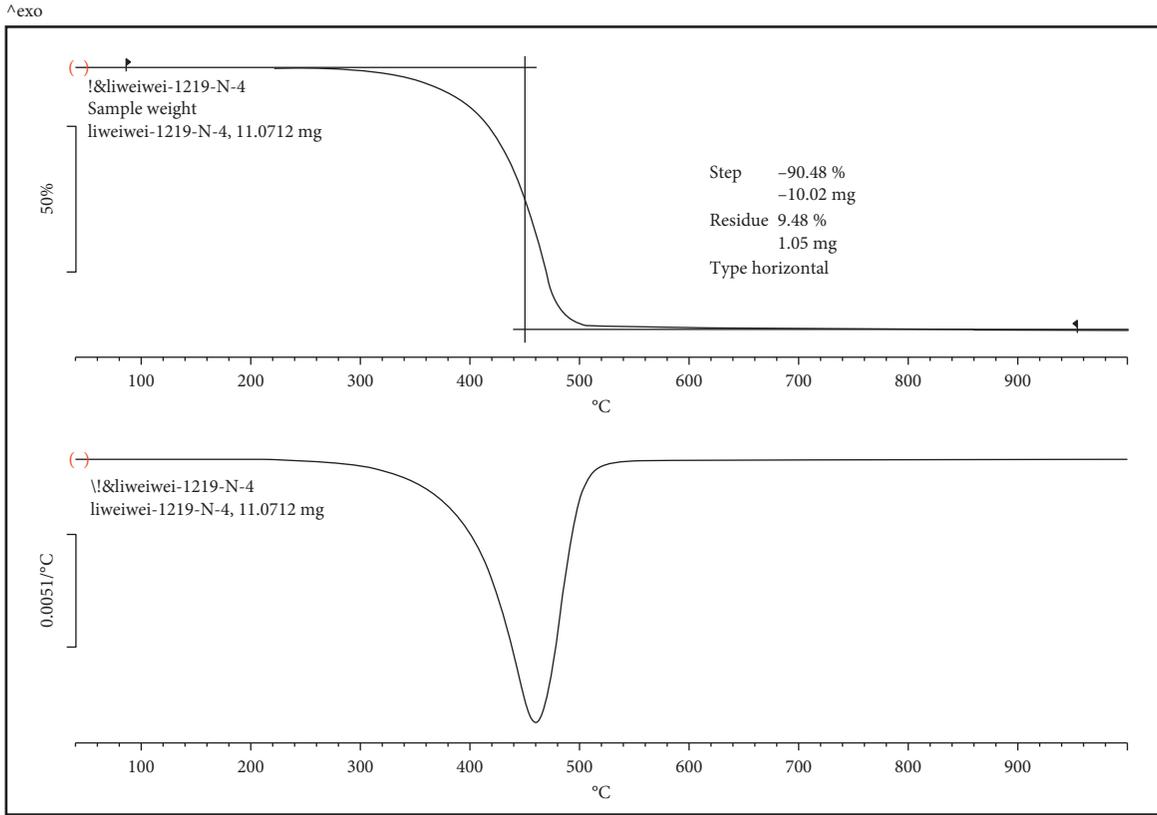
3.1.2. Effects of Aging on the Chemical Properties of SBS-Modified Asphalt

(1) FTIR Tests. The aging process of SBS-modified asphalt is essentially a slow process of chemical reaction. A shift of

functional groups inevitably accompanies the chemical reaction of organic matters. In the infrared spectrogram, the absorption band spectra shown are also different. Figure 3 contains the infrared spectrograms of SBS-modified asphalt before and after aging in room temperature conditions.

In general, the stretching vibration absorption peak of hydroxyl is at 3450 cm^{-1} , mainly characterized by a wide peak and that the higher degree of association, the closer the peak to low wavenumber; the stretching vibration absorption peak of alkyl hydrocarbon bonds is at $2800\text{ cm}^{-1}\sim 3000\text{ cm}^{-1}$, including $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{CH}$; carbonyl absorption peaks in ketone and carboxylic acid are near 1600 cm^{-1} . When the carbonyl group and a benzene vibrate, the absorption peak moves towards the low wavenumber. The bending vibration absorption peak of alkyl hydrocarbon bonds is at $1350\text{ cm}^{-1}\sim 1480\text{ cm}^{-1}$, including $-\text{CH}_3$ (1370 cm^{-1} and 1450 cm^{-1}), $-\text{CH}_2$ (1465 cm^{-1}), and $-\text{CH}(\text{CH}_3)_2$ ($1365\text{ cm}^{-1}\sim 1385\text{ cm}^{-1}$); the stretching vibration absorption peak of organic sulfoxide and sulphone is at $1120\text{ cm}^{-1}\sim 1160\text{ cm}^{-1}$ and $1030\text{ cm}^{-1}\sim 1070\text{ cm}^{-1}$; the C-H bond out-of-plane bending vibration absorption peak of olefins (polybutadiene) is at $900\text{ cm}^{-1}\sim 950\text{ cm}^{-1}$; the C-H bond out-of-plane bending vibration absorption peak of a series of heteroaromatic compounds is at $650\text{ cm}^{-1}\sim 810\text{ cm}^{-1}$, whereas the C-H bond out-of-plane bending vibration absorption peak of benzene rings of styrene and fatty aldehyde is at 700 cm^{-1} . Asphalt mainly consists of elemental carbon, hydrogen, oxygen, nitrogen, and sulfur. The infrared spectrogram shows that, with the increase of the aging period, the absorption intensity of different groups has different degrees of increase and decrease. These long-chain polymers often contain carbon-carbon double bonds and carbon-carbon triple bonds, which are very unstable and easily have addition reaction or oxidation reaction to produce hydroxyl groups and carbonyl groups. Some hydroxyl groups, due to the chain end effect, will be further oxidized to produce ketone or carboxylic acid.

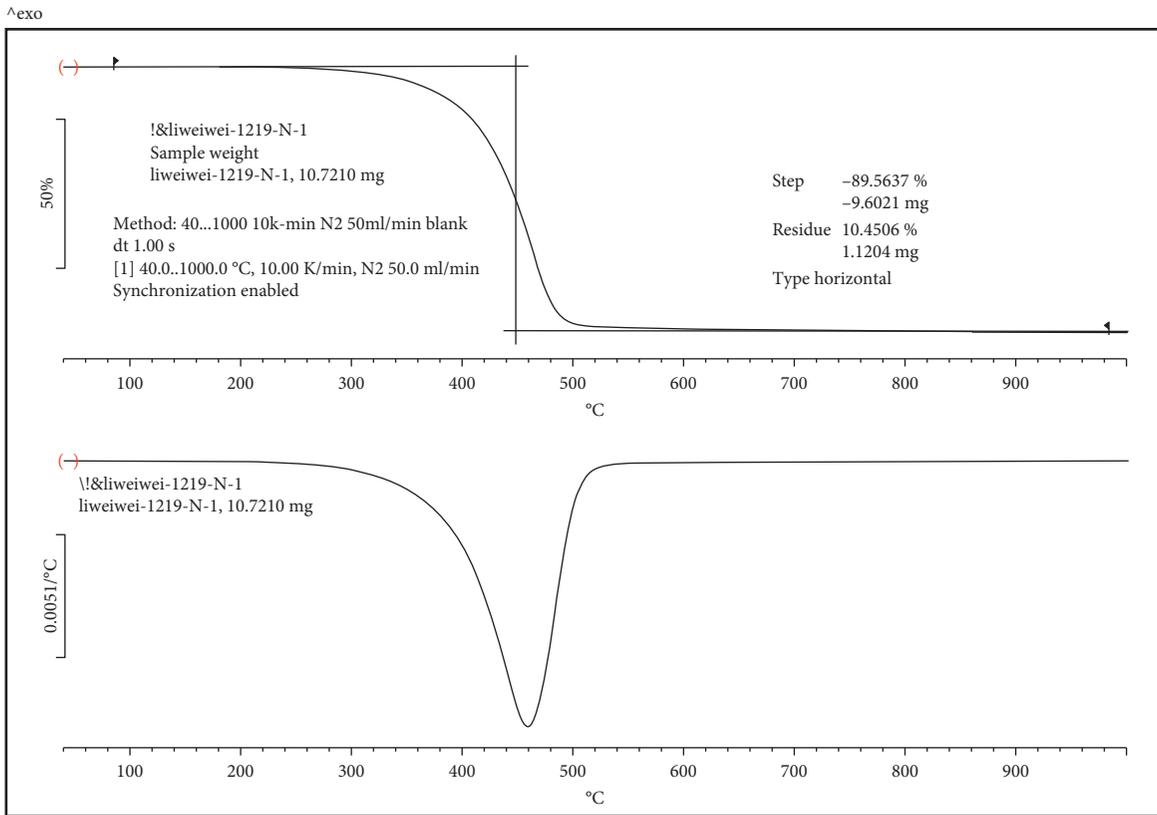
After aging of SBS-modified asphalt, a new absorption peak appears at $1120\text{ cm}^{-1}\sim 1160\text{ cm}^{-1}$ and $1030\text{ cm}^{-1}\sim 1070\text{ cm}^{-1}$. This is because elemental sulfur in the modified asphalt is oxidized to sulfoxide (S=O) and sulphone (O=S=O). The absorption intensity of the two absorption peaks increases with the aging time of asphalt. Sulfur mainly exists in the form of sulfur ether and mercaptan in asphalt molecules. Peroxide easily oxidizes sulfur ether and mercaptan into sulfoxide base, a sulfur atom which still has a pair of lone electrons. In the case of sufficient oxygen, sulfoxide groups will be further oxidized into sulfonates. In addition to such polar functional groups as ketones, aldehydes, and carboxyl, a series of heteroaromatic compounds are also produced in the aging of SBS-modified asphalt. These heteroaromatic compounds are from the cleavage oxidation and local cleavage polymerization of SBS polystyrene chain segments. The deeper the asphalt is aged, the higher the heteroaromatic compound's absorption intensity is, indicating a higher decomposition degree of polystyrene.



Lab: METTLER

STAR® SW 14.00

(a)



Lab: METTLER

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(b)

FIGURE 2: TG curve of aged SBS-modified asphalt. (a) Before aging. (b) After aging.

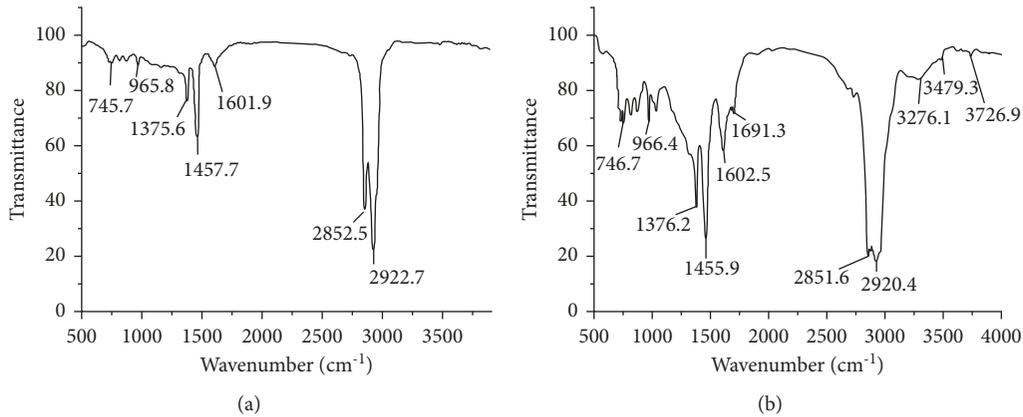


FIGURE 3: Infrared spectrogram of SBS-modified asphalt. (a) Before aging. (b) After aging.

Infrared spectroscopy shows that the reason for the embrittlement and hardening of SBS-modified asphalt after aging is SBS failure and the generation of a large number of polar groups. Polar groups have strong intermolecular interaction, and some form an association body, which reduces asphalt ductility and increases stiffness modulus.

(2) *NMR Tests.* Figure 4 shows the nuclear magnetic resonance spectrograms of SBS-modified asphalt before and after aging. The peak at 1 ppm-2 ppm belongs to hydrogen on methyl in the sample, and the one at 3.7 ppm belongs to hydrogen on methene (alkene) and methine (alkyne). Comparison between the two figures shows that the characteristic peaks of methene and methine at 3.7 ppm have disappeared in the nuclear magnetic resonance spectrogram of SBS-modified asphalt after aging. The reason is that, with the progress of aging, the double bonds of SBS polybutadiene segments are opened when oxidation occurs. Some double bonds are oxidized into alcoholic hydroxyl groups, carbonyl groups, or carboxyl groups, and some are added to produce saturated carbon bonds; some small molecules may also have mutual addition to producing macromolecules with unsaturated carbon-carbon bonds, namely, alkyl produced by alkene or alkyne through hydrogenation (generally oxygen addition).

In the nuclear magnetic resonance spectrogram of SBS-modified asphalt after aging, the characteristic peaks of methene and methine at 3.7 ppm have disappeared, indicating that SBS decomposition and degradation have completed.

3.1.3. Effects of Aging on the Surface Microtopography of SBS-Modified Asphalt. The SEM images of SBS-modified asphalt before and after aging are shown in Figures 5(a) and 5(b).

Figure 5(a) shows that the SBS asphalt is uniform. It indicates that modifier SBS can be evenly distributed in asphalt to form a subhomogeneous island structure; namely, styrene-butadiene-styrene triblock forms a network structure in the base asphalt. Figure 5(b) shows the SEM image of SBS-modified asphalt after aging. Observed under SEM, it is

very homogeneous, with few impurities in local parts, and the subhomogeneous island structure has disappeared. It is inferred that SBS has had severe cracking and decomposition and produced small molecules, or has had oxygen absorption reaction and produced highly polar substances. This coincides with the results of the GPC test above.

3.1.4. Effects of Aging on the Elementary Composition of SBS-Modified Asphalt. The analysis results of the SEM-EDS of SBS-modified asphalt before and after aging are shown in Table 1.

As shown in Table 1, the C content of aged SBS-modified asphalt has decreased compared with that of original SBS-modified asphalt, while the O content and S content have increased obviously. According to analysis, the reason is that, with the deepening of aging, sulfur elements in modified asphalt were oxidized into sulfoxide (S=O) and sulphone (O=S=O). In addition to such polar functional groups as ketones, aldehydes, and carboxyl, a series of heteroaromatic compounds are also produced in the aging of SBS-modified asphalt. These heteroaromatic compounds are from the cleavage oxidation and local cleavage polymerization of SBS polystyrene chain segments. The deeper the asphalt is aged, the higher the heteroaromatic compound's absorption intensity is, indicating a higher decomposition degree of polystyrene. These long-chain polymers often contain carbon-carbon double bonds and carbon-carbon triple bonds, which are very unstable and easily have addition reaction or oxidation reaction to produce hydroxyl groups and carbonyl groups. Some hydroxyl groups, due to the chain end effect, will be further oxidized to produce ketone or carboxylic acid.

3.2. Recycling of Aged SBS-Modified Asphalt

3.2.1. Effects of Rejuvenators on the Basic Properties of Aged SBS-Modified Asphalt. In this section, the effect of the two rejuvenators on the macroproperties of aged SBS-modified asphalt was explored. The contents of rejuvenators were 6%, 8%, 10%, 12%, and 14% of base asphalt binder by mass.

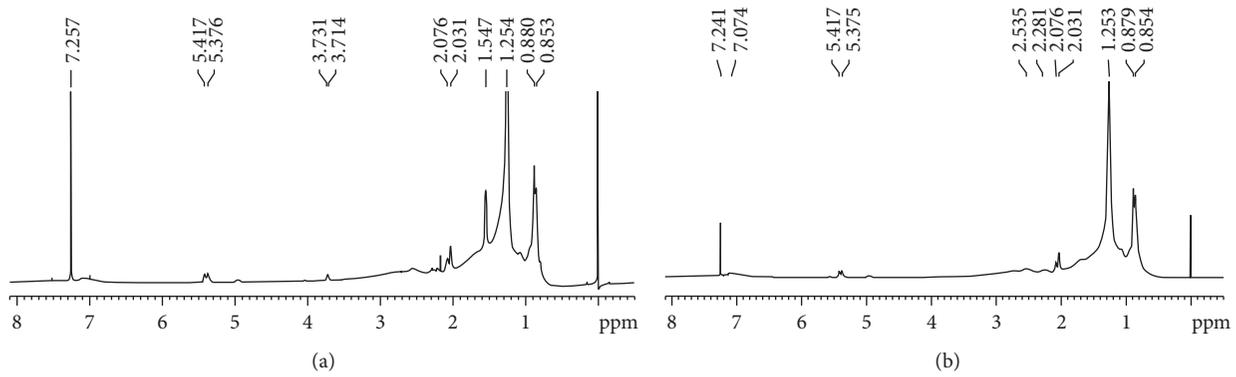


FIGURE 4: Nuclear magnetic resonance spectrograms of SBS-modified asphalt. (a) Before aging. (b) After aging.

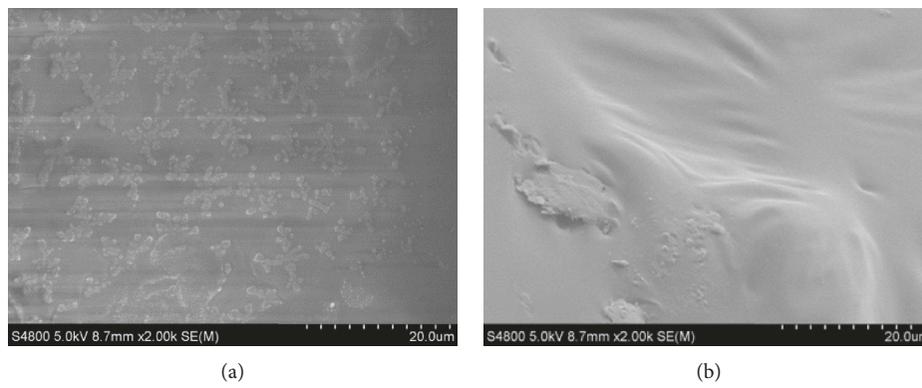


FIGURE 5: SEM images of SBS-modified asphalt. (a) Before aging. (b) After aging.

TABLE 1: Effects of aging on the elementary composition of SBS-modified asphalt.

Element type	Element content of SBS-modified asphalt (%)	
	Before aging	After aging
C	90.0	62.2
O	7.4	22.5
S	0.8	1.1

(1) *Viscosity*. Figure 6 shows the changes in the viscosity of aged SBS-modified asphalt after epoxy resin rejuvenators A and B are added. According to the figure, the viscosity of aged SBS-modified asphalt decreases with the increase of the additive amount of the epoxy resin rejuvenators A and B. This is because these two rejuvenators contain both low-viscosity catalytic cracking oil slurry and epoxy functional group compounds, whose viscosity is lower than that of SBS-modified asphalt, and it makes the viscosity of recycled SBS-modified asphalt decreases with the increasing additive amount of rejuvenator. The rejuvenators A and B have different effects on the viscosity of aged SBS-modified asphalt. The viscosity of asphalt modified by rejuvenator A is lower than that modified by rejuvenator B. According to the molecular structures of the two rejuvenators, the molecular backbone of rejuvenator A is a flexible aliphatic, while that of rejuvenator B is a rigid benzene ring structure. It leads to that

viscosity of asphalt modified by rejuvenator A is lower than that modified by rejuvenator B.

(2) *Penetration*. Figure 7 shows the penetration improvement of the aged SBS-modified asphalt after the epoxy resin recycling agents A and B are added. According to the figure, the penetration of recycled SBS-modified asphalt increased with the increase of the content of the recycling agent. We speculate that the reason is that these two recycling agents contain both low-viscosity catalytic cracking oil slurry and epoxy functional group compounds, whose viscosity is lower than that of SBS-modified asphalt, and it makes the penetration of recycled SBS-modified asphalt decreases with the increasing additive amount of recycling agent.

Regarding the molecular structure, the molecular backbone of recycling agent A is a flexible aliphatic, while that of recycling agent B is a rigid benzene ring structure. However, recycling agent B does not recover to the triblock molecular chain structure of SBS, so the effect of recycling agent B on the penetration of aged SBS-modified asphalt is not as evident as that of recycling agent A.

(3) *Ductility*. Figure 8 shows the effects of recycling agents A and B on the ductility of aged SBS-modified asphalt.

It can be seen from Figure 8 that the ductility of aged SBS-modified asphalt increased with the increasing additive amount of recycling agent A. The possible reason was that

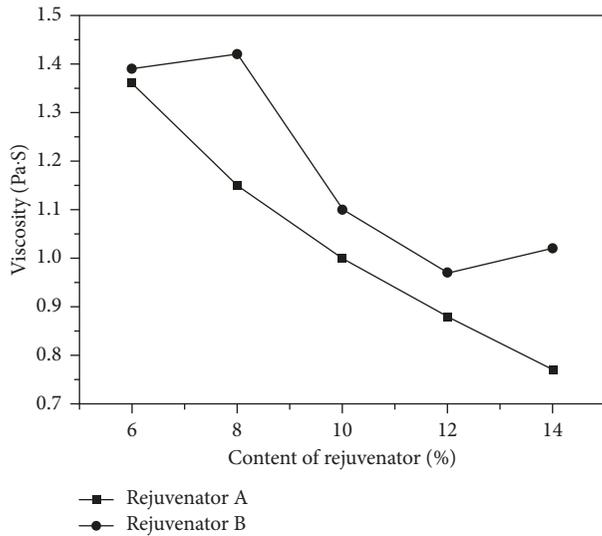


FIGURE 6: Effect of rejuvenators A and B on a viscosity of aged SBS-modified asphalt binder.

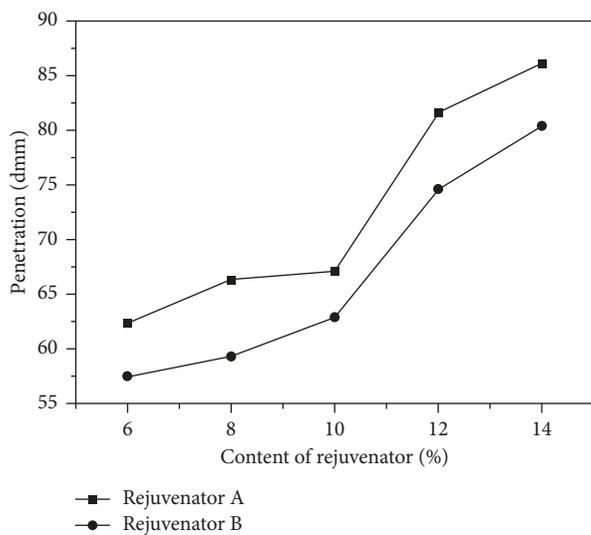


FIGURE 7: Effect of rejuvenators A and B on the penetration of aged SBS-modified asphalt binder.

the epoxy functional groups of recycling agent A reacted with the cracked carboxyl at the SB molecular chain end. It made biblock copolymer SB re-crosslinked into triblock copolymer SBS by epoxy resin molecular chains. That is, the triblock molecular structure of SBS was recovered, with the macro performance that the ductility of aged SBS-modified asphalt was obviously recovered. Recycling agent B did not have the recovered triblock molecular chain structure of SBS, so the addition of recycling agent B had an insufficient effect on the ductility of aged SBS-modified asphalt.

(4) *Softening Point.* The softening point improvement of the aged SBS-modified asphalt after the epoxy resin recycling agents A and B are added is shown in Figure 9.

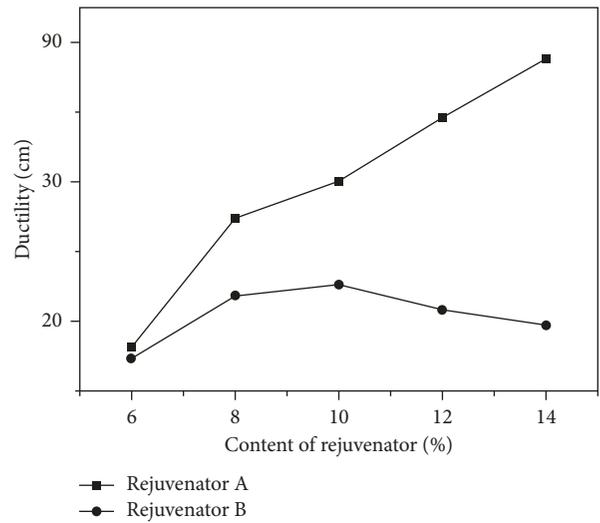


FIGURE 8: Effect of rejuvenators A and B on the ductility of aged SBS-modified asphalt binder.

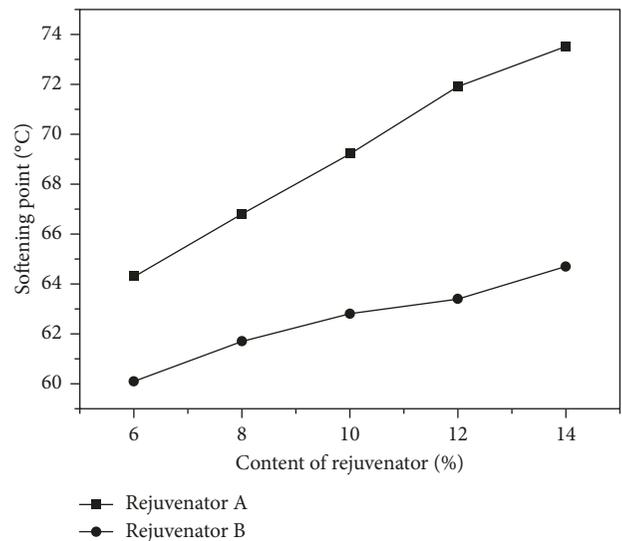


FIGURE 9: Effect of rejuvenators A and B on the softening point of aged SBS-modified asphalt binder.

According to Figure 9, the softening point of recycled SBS-modified asphalt rises with the increasing additive amount of recycling agent. Compared with recycling agent B, the softening point rises more sharply by adding recycling agent A because recycling agent A recovers the triblock molecular structure of SBS and accelerates the rising trend of the softening point. Although recycling agent B has a low-viscosity component, it does not recover the molecular chain structure of SBS, resulting in a very limited increase of softening point.

3.2.2. *Effects of Rejuvenators on the Molecular Weight Distribution of Aged SBS-Modified Asphalt.* The GPC graphs of SBS-modified asphalt after rejuvenators A and B are added are shown in Figure 10.

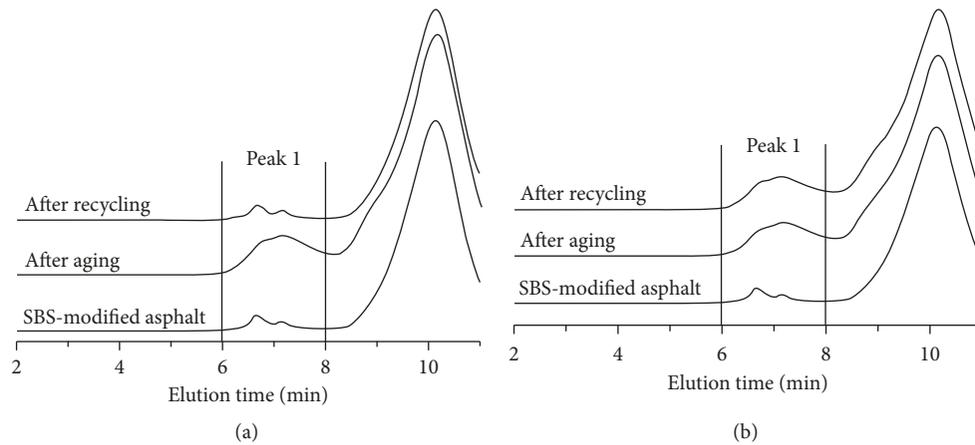


FIGURE 10: Effect of aging and recycling on molecular weight distribution of SBS-modified asphalt binder. (a) Rejuvenator A. (b) Rejuvenator B.

According to Figure 10, the SBS molecular chain cracks after the aging of SBS-modified asphalt, which is characterized by the trailing in the macromolecular part at Peak 1 of the GPC curve. After recycling agent A is added, the GPC curve at Peak 1 has migrated overall; that is, the previous macromolecular chain is recovered. It is inferred that the epoxy functional groups of recycling agent A react with the cracked carboxyl at the SB molecular chain end, which makes diblock copolymer SB re-crosslinked into triblock copolymer SBS by epoxy resin molecular chains. That is, the triblock molecular structure of SBS is recovered. After recycling agent B is added, the GPC curve at Peak 1 has no noticeable change. It indicates that epoxy functional groups of recycling agent B did not have coupling reaction with the SB molecular chain end, resulting in the very limited effect on the recycling of SBS-modified asphalt.

3.2.3. Effects of Rejuvenators on the Microstructure of Aged SBS-Modified Asphalt

(1) *Fluorescence Microscope.* Figures 11(a) and 11(b) show the microscopic morphology of SBS-modified asphalt recycled by adding the epoxy resin recycling agents A and B, respectively. Under a fluorescence microscope, SBS is the bright area in the figure. In Figure 11(b), there are very few particles in the bright area, and it is inferred that serious chain fracture occurred in the SBS triblock copolymer after asphalt aging, indicating serious aging of SBS. Figures 11(a)–(C) show the aged SBS-modified asphalt after recycling agent A is added. According to the figure, the distribution of bright area has been obviously improved and is close to that before aging. It indicates that the recycling agent A has obviously restored the SBS distribution and thus improved the aging degree of SBS-modified asphalt. Figures 11(b)–(C) show that SBS distribution has no obvious changes after recycling agent B is added, indicating very limited recycling effect. The microproperties are consistent with the molecular weight result tested by GPC.

Therefore, the recycling agent A has an obviously better recycling effect than the recycling agent B.

(2) *SEM.* The microscopic morphologies of SBS-modified asphalt recycled by adding the epoxy resin recycling agents A and B are shown in Figures 12(a) and 12(b), respectively.

It can be seen from Figures 12(a)–(A) and 12(b)–(A) that SBS is distributed in the base asphalt, which can be called the island structure in the SEM image. With the progress of aging, serious chain fracture occurs in the SBS triblock copolymer, which is manifested by the missing of islands in Figure 12(a)–(B). Figure 12(a)–(C) shows the aged SBS-modified asphalt after recycling agent A is added. According to the figure, the islands are recovered and similar to those before aging. It indicates that the rejuvenator A has obviously restored the SBS triblock structure and thus improved the aging degree of SBS-modified asphalt. Figure 12(a)–(A) shows that the SEM image has no obvious changes after rejuvenator B is added, indicating a very limited recycling effect. The microproperties are consistent with the molecular weight result tested by GPC and fluorescence microscopy results. The rejuvenator A has higher reactivity and better recycling effect than rejuvenator B.

4. Conclusions

Based on the testing and analysis presented in this paper, the conclusions of the study are summarized as follows:

- (1) Infrared spectrogram analysis results show that, with the aging progress of asphalt, the area of the carbonyl absorption peak and carbonyl content increase continuously; sulfur compounds in asphalt react with oxygen to produce sulfoxide base functional groups during asphalt aging. The butadiene absorption peak gradually disappears, indicating that base asphalt components and SBS copolymer age simultaneously during asphalt aging; with the degradation of the SBS copolymer, the reticular

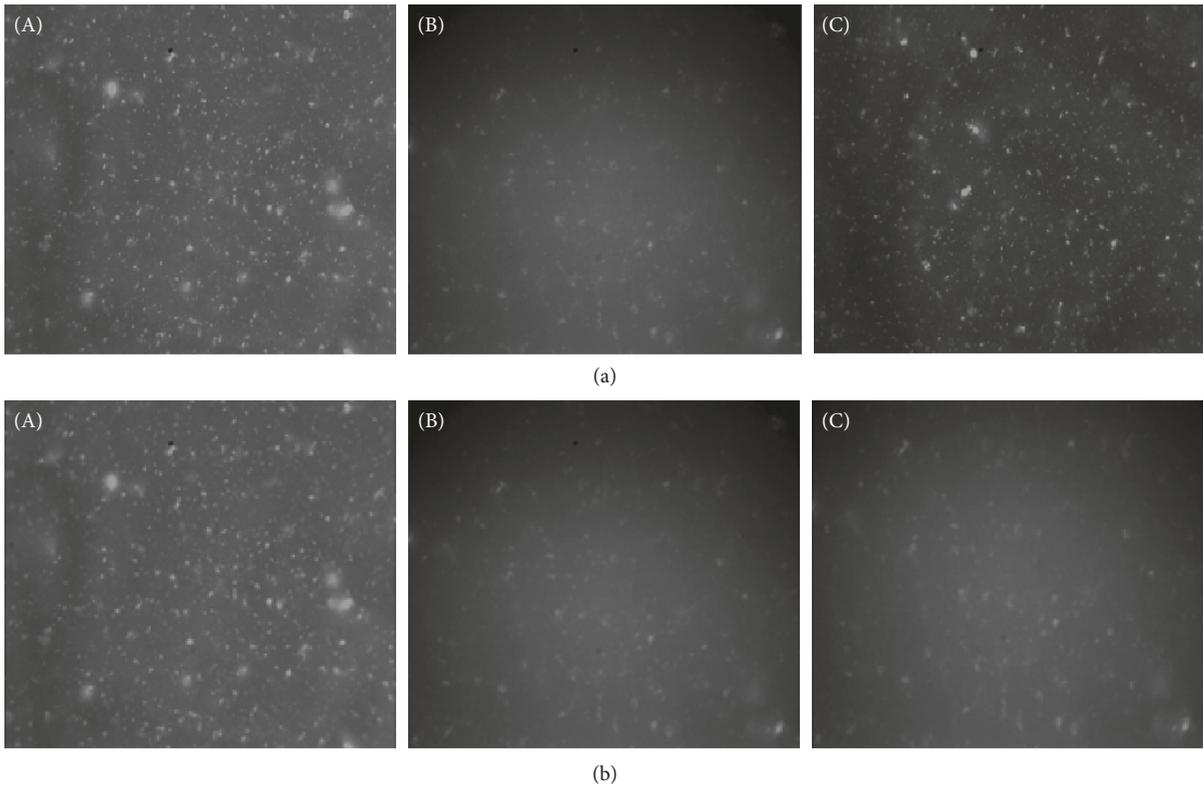


FIGURE 11: Effect of rejuvenators on microstructure of aged SBS-modified asphalt binder by fluorescence microscope (measuring scale is 1 : 10000): (A) SBS-modified asphalt, (B) aged SBS-modified asphalt, and (C) recycled SBS-modified asphalt of (a) rejuvenator A and (b) rejuvenator B.

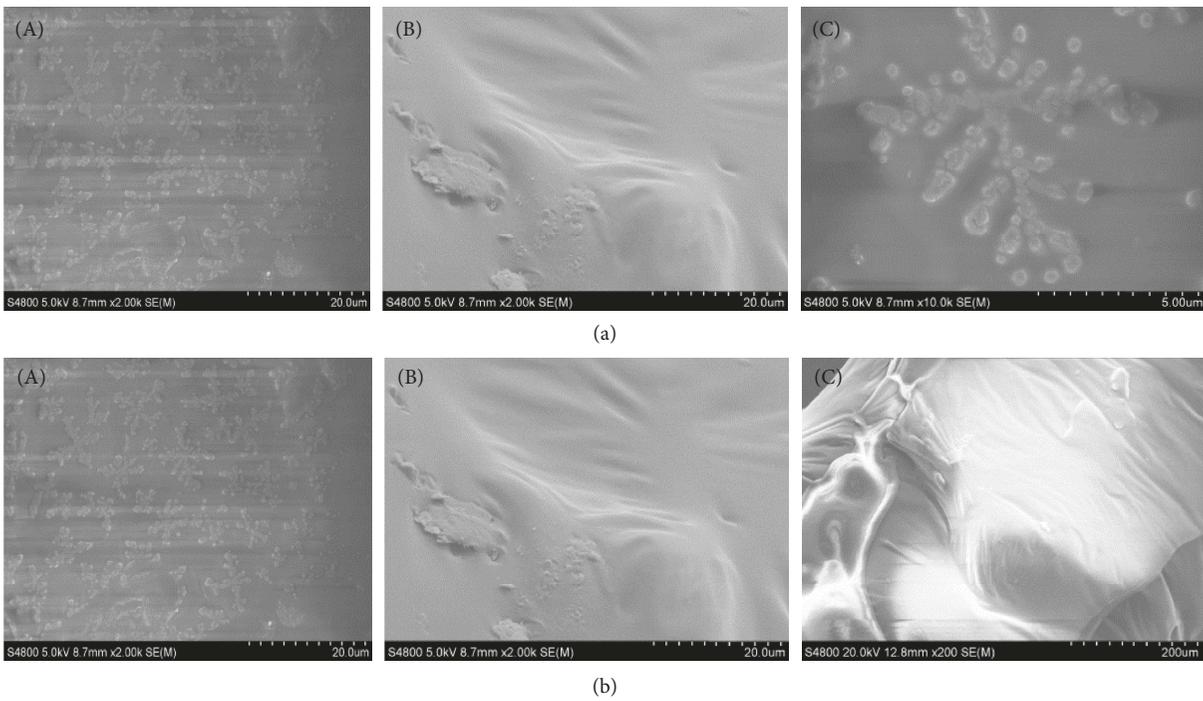


FIGURE 12: Effect of rejuvenators on microstructure of aged SBS-modified asphalt binder by SEM: (A) SBS-modified asphalt, (B): aged SBS-modified asphalt, and (C): recycled SBS-modified asphalt of (a) rejuvenator A and (b) rejuvenator B.

crosslinking structure of asphalt is destroyed and SBS's modification effect is gradually lost. The increase of polar functional groups of SBS-modified asphalt and the decomposition and failure of the SBS modifier are the immanent causes for continuous change in viscosity, strengthening of high-temperature performance, and reduction of low-temperature anticrack property.

- (2) According to the SEM analysis results, modifier SBS can be evenly distributed in asphalt to form a sub-homogeneous island structure; namely, styrene-butadiene-styrene triblock forms a network structure in the base asphalt. According to the SEM image of SBS-modified asphalt after aging, observed under SEM, it is very homogeneous, with few impurities in local parts, and the subhomogeneous island structure has disappeared. It is inferred that SBS has had severe cracking and decomposition and produced small molecules, or has had oxygen absorption reaction and produced highly polar substances. Energy spectrum analysis shows that, with the progress of aging, the C content of aged SBS-modified asphalt has decreased compared with that of original SBS-modified asphalt, while the O content and S content have increased obviously.
- (3) Fluorescence microscope and SEM were used to observe the changes in molecular structure and distribution of the SBS modifier before and after recycling. It shows that the epoxy functional group compounds of aliphatic glycidyl ether resin have high reactivity, and the triblock molecular structure of SBS is recovered. The pavement performance of recycled SBS-modified asphalt also shows that it has a good recycling effect. GPC demonstrated that epoxy functional groups of recycling agent B did not have coupling reaction with the SB molecular chain end, resulting in the very limited effect on the recycling of SBS-modified asphalt.

Based on the findings of this research, chemical-related tests are recommended conducting to select one proper rejuvenator for the aged SBS-modified asphalt. This can increase recycling efficiency.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Meng Guo and Daisong Luo conceived and designed the experiments. Meng Guo performed the experiments. Liantong Mo and Meng Guo analyzed the data. Yiqiu Tan

and Yafei Li contributed reagents/materials/analysis tools. Yubo Jiao and Asim Farooq wrote the paper.

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