

Research Article

Microscopic Analysis of the Rejuvenation Mechanism and Rejuvenation Effect of Asphalt Binders

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This study investigates the rejuvenation mechanism of asphalt binders at the microscopic level and compares the rejuvenation effects of rejuvenators. A model of rejuvenated asphalt was established on the basis of molecular simulation by adding different doses of two rejuvenators to the aged asphalt. This model was validated in terms of density and surface free energy. The diffusion ability of the rejuvenator was investigated by using a diffusion model and mean square displacement. The deagglomeration ability of rejuvenators on asphaltene was explored by using a radial distribution function. The microscopic mechanism of asphalt rejuvenation was explained. Results show that small molecule structures are more diffusible than long-chain structures, and aromatic ring structures are more attracted than polar functional groups. The rejuvenating effect of the rejuvenator was evaluated in terms of viscosity and cohesive energy density. Results show that the long-chain structure reduces the viscosity value more than the small molecule structure. The aromatic ring structure in the aged asphalt helps to restore the compatibility between the fractions. This study serves as a guide for the selection and development of future rejuvenators.

1. Introduction

Asphalt mixture is a material commonly used for pavement laying. Under the combined action of sunlight, water, and the atmosphere, asphalt pavements become hard and brittle and suffer from various types of damage, shortening the service life of the pavement [1]. Waste asphalt mixtures that have exceeded their service life are often restored through hot recycling technology and reused for pavement placement to solve this pavement aging problem [2, 3]. The hot rejuvenation technology has good environmental and economic benefits, but its implementation is an important engineering challenge. The solution to this problem is to understand the mechanisms inherent in the rejuvenation process of the asphalt.

The rejuvenation process of asphalt mixtures usually involves changes in the proportion and material composition of the four components of aged asphalt [4]. The aging and rejuvenation process of asphalt involves a series of

physicochemical changes at the microscopic level [5]. These changes include the flow and diffusion of asphalt fractions and the oxidation and condensation reactions of the fractions. The specific changes in the asphalt fraction during this process are difficult to describe quantitatively through practical experiments [6]. The effect of the rejuvenator on the aging asphalt is influenced by its microstructure [7]. Dissimilar molecular structures may lead to incompatibility between asphalt and rejuvenator and asphaltene agglomeration to form precipitates [8]. Therefore, microlevel analysis of asphalt rejuvenation is needed in the study of asphalt mixture rejuvenation.

Microscopic analysis of asphalt includes practical tests, such as Fourier infrared spectroscopy, atomic force microscopy, and gel permeation chromatography [9]. These experiments are often related to structural analysis and do not directly reflect the performance of the rejuvenator and asphalt during use. Molecular simulation as a microscopic research method has an important role in the analysis and

prediction of material properties [10]. This simulation accurately calculates the characteristic parameters of the molecule in the system by selecting the appropriate force field for the corresponding system. The simulated motion of molecules can reflect the microscopic properties of real materials [11]. A dynamic change occurs in the structure and properties of the asphalt after the addition of the rejuvenator. Static analytical experiments cannot clearly demonstrate this process. Therefore, molecular dynamics simulation is a better choice for studying the mechanism during the mixing process of asphalt and rejuvenator and analyzing the performance change after rejuvenation.

This study focuses on two structures, fatty acids and aromatic rings, for the microscopic molecular simulation of the rejuvenation mechanism of aged asphalt. The diffusion ability of the added rejuvenator in aged asphalt was evaluated in terms of the diffusion effect of the rejuvenator at different stages. The ability of the rejuvenator to deagglomerate asphaltene was assessed by using a radial distribution function (RDF). The rejuvenation mechanism is reflected in terms of the diffusion and deagglomeration ability. The viscosity of aged asphalt models with different rejuvenators added at different temperatures was calculated through molecular simulation to compare the performance changes of aged asphalt before and after rejuvenation. The compatibility of the two rejuvenators and asphalt was analyzed in terms of cohesive energy density (CED), which reflects the rejuvenating effect of the rejuvenator. The results reflect the improvement effect of the rejuvenator on the aged asphalt and the microscopic rejuvenation mechanism of the rejuvenator.

2. Molecular Simulation

2.1. Molecular Simulation Technology. Molecular simulation is an important research method in materials science. This technique includes Monte Carlo and kinetic methods. Molecular structures and atomic types are simulated to represent their actual physical and chemical properties. Molecular simulation has the advantages of saving time and materials, high accuracy, and safety compared with actual tests. With the development of computers and computational theories, the accuracy of molecular simulations is increasing. The use of this technique to simulate molecular evolution and predict actual tests has become an important tool in materials science. Molecular simulation will be an indispensable research technique in the study of asphalt materials in the future [12]. The visualization can accurately reflect the entanglement and connection pattern between the fractions of asphalt. In this study, a dynamics study in molecular simulation is used. The kinetic study mainly relies on the integral calculation under Newtonian mechanics to realize the thermodynamic and property transfer between models in various configurations. This study demonstrates the rejuvenation mechanism of rejuvenators in aged asphalt and predicts the property changes of asphalt under the rejuvenation effect by microscopically simulating the movement of asphalt fractions. Modeling and calculations are performed on Materials Studio 2019. The force field is chosen as COMPASSII, which can better reflect a complex

molecular system, such as asphalt [13]. Geometry optimization and annealing in the Forcite module are used for geometric optimization and annealing of the asphalt model, and subsequent dynamics simulations are performed on Dynamics. The time step in the dynamic simulation is set to 1 fs. The summation is calculated by using atom-based summation, and the mass is chosen as fine. Therefore, the truncation distances on the molecules are all set to 15.5 Å.

2.2. Modeling of Asphalt

2.2.1. Molecular Model of Asphalt. Asphalt is a substrate product of the petroleum industry and consists of a large number of substances with complex structures. It often contains polycyclic aromatic hydrocarbons, heterocycles with heteroatoms, acids, and phenolic compounds. Therefore, the molecular structure has a large variation in the carbon to hydrogen ratio and contains some electronegative atoms, such as oxygen, nitrogen, and sulfur. Existing component theory relies on molecular weight and solubility to divide asphalt into four components, namely, saturates, aromatics, resins, and asphaltenes [14]. The asphalt can be further divided into 12 components containing different structures. In this study, the commonly used AAA-1 model is used [15], which is a representative 12-component model. The aging effect is an important factor that should be considered when modeling asphalt. Under the long-term action of oxygen in the air, the asphalt fraction is subjected to oxidation, thereby increasing the concentration of oxygen atoms. On the basis of the AAA-1 model, an oxidized AAA-1 model for simulated oxidation effect is proposed to simulate aging asphalt [16]. Typical oxidation groups, such as ketones and sulfoxide groups, are incorporated into the molecular structure to represent aging effects [17]. Taking asphaltene as an example, the corresponding joining position is shown in Figure 1, where the saturation fraction is modeled to be constant before and after aging. Table 1 shows the proportions of the fractions in the aged asphalt and the corresponding number of molecules incorporated in the model.

2.2.2. Confined Model and Bilayered Model. A confined model is used to calculate the surface free energy, and a bilayered model is used to study the diffusion of the rejuvenator. The diffusion of the rejuvenator in aged asphalt is a physical process [5]. The result of diffusion affects the extent in which the rejuvenator can play a role. The reduction in viscosity and the increase in diffusion ability are mutually reinforced [18]. Lower viscosity can accelerate the diffusion, and better diffusion can effectively reduce the viscosity. In this study, an asphalt bilayered model was developed to study the diffusion ability of the rejuvenator, as shown in Figure 2. The volume and density of the rejuvenator model layer were made the same as those of the asphalt model layer, and then the two layers were assembled. A vacuum layer of 5 Å was reserved between the two layers. The assembled model was geometrically optimized and annealed to obtain the lowest stable energy of the initial model. Diffusion simulation of the model was conducted at hot mixing

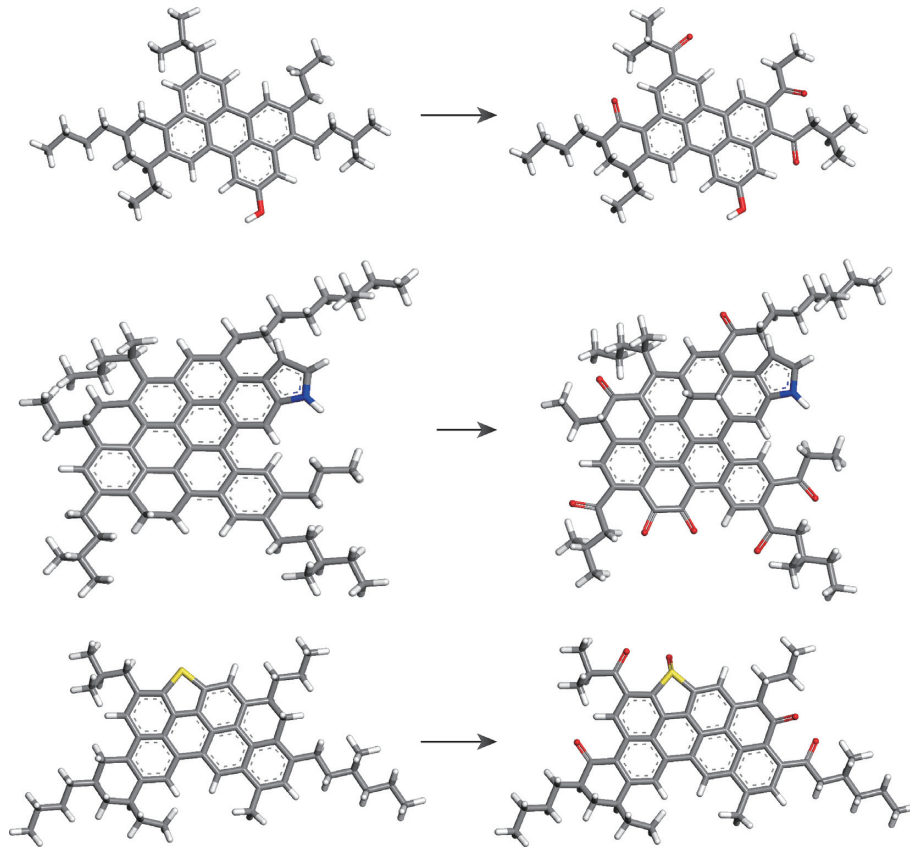


FIGURE 1: Corresponding positions of the oxidation functional groups introduced in the AAA-1 asphaltene model (red for oxygen atoms, blue for nitrogen atoms, and yellow for sulfur atoms).

TABLE 1: Proportion of fractions and the number of corresponding molecules of aged asphalt.

Fractions	Molecular formula	Number	Mass fraction
Asphaltene	$C_{42}H_{54}O$	3	19.3
	$C_{66}H_{83}N$	3	
	$C_{51}H_{62}S$	4	
Resin	$C_{36}H_{57}N$	6	36.4
	$C_{40}H_{60}S$	5	
	$C_{18}H_{10}S_2$	6	
	$C_{40}H_{59}N$	7	
	$C_{29}H_{50}O$	15	
Aromatic	$C_{35}H_{44}$	9	16.5
	$C_{30}H_{46}$	9	
Saturate	$C_{30}H_{62}$	10	27.8
	$C_{35}H_{62}$	9	

temperature (433 K). A constant temperature and pressure simulation of 100 ps was performed in the isothermal-isobaric ensemble. This operation was designed to shrink the volume to a preequilibrium state. The molecules of the rejuvenator and the asphalt molecules have sufficient time to come into contact and to mix initially. A constant temperature isovolume simulation of 2 ns was performed in the canonical (NVT) ensemble. During this process, the rejuvenator and asphalt molecules were mixed to a great extent. Density and diffusion depth results were used to evaluate the diffusion ability of the two rejuvenators.

2.3. Model Validation

2.3.1. Density. Density is an important physical parameter of asphalt and reflects its consistency [19]. Molecular simulation can be used to verify the correlation between the model and the actual experiment. In this study, the initial density of the model was set to 1.0 g/cm^3 . The model shrinkage has reached an equilibrium by performing a 500 ps NPT dynamics simulation on this model. The steady density generated in this state was taken for analysis.

The calculated densities are shown in Table 2. The density of the aged asphalt model is slightly higher than the density of virgin asphalt. This finding is consistent with the results that usually occur in practice.

2.3.2. Surface Free Energy. Surface free energy reflects the ability of the asphalt to crack and form a new surface. Higher energy reflects the increased brittleness of the asphalt [20]. Asphalt becomes hard and brittle after aging, which is a manifestation of the improved rutting resistance of asphalt. However, this condition is accompanied by a reduction in the deformability of the asphalt. The surface free energy of asphalt in molecular simulations was measured by using a confined model. The calculation formula is shown in the following equation:

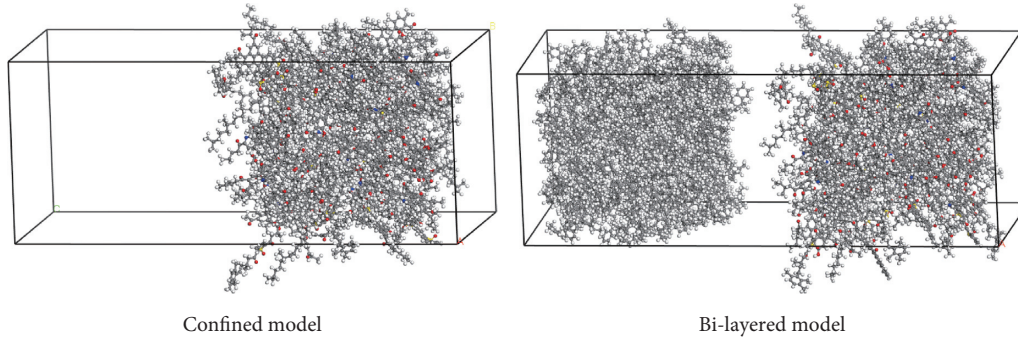


FIGURE 2: Confined model and bilayered model.

TABLE 2: Simulation validation of virgin and aged asphalt properties.

Properties	Virgin asphalt	Aged asphalt	Results
Density (g/cm ³)	0.973	1.005	0.95–1.08 [21]
Surface free energy ((J/cm ³) ^{1/2})	18.21	19.73	13.3–22.5 [20]

$$\gamma_a = \frac{(E_{\text{film}} - E_{\text{bulk}})}{2A}, \quad (1)$$

where γ_a is the surface free energy, E_{film} and E_{bulk} represent the potential energy of the confined model and the bulk model, and A is the area of the new surface. The potential energy results were generated after the 500 ps NVT dynamics simulation at 298 K. The calculation results are shown in Table 2. The results show that the surface free energy of aged asphalt is higher than that of virgin asphalt. This finding confirms that aging makes asphalt brittle.

2.4. Rejuvenator Molecular Model. Rejuvenators are used to improve the performance of aged asphalt. They can be obtained from a variety of sources, including animal and vegetable oils and thread-reducing oils [22]. Therefore, rejuvenators in actual use contain complex molecular structures. On the basis of the structure type, rejuvenators are usually classified as aromatic extracts, tall oils, fatty oils, and petroleum-based substances [23]. Various oil rejuvenators play different roles in aging asphalt. Molecular dynamics simulation studies show that a synergistic effect is found between wax oil and asphaltene, thereby improving the fluidity [24]. The addition of waste vegetable oil improves the rutting, fatigue, and thermal cracking resistance of asphalt [25]. Crude palm oil is used as a biorejuvenator to improve the tensile strength of aged asphalt [26]. The molecular structure is improved during the blending process by mixing coal tar pitch with petroleum asphalt for modification [27].

However, all of these rejuvenators contain a complex structural composition of fractions, forming a huge system in the molecular simulation, which is un conducive to research and analysis. From the point of view of the widely used commercial rejuvenators, the molecular structure of rejuvenators can be summarized as long-chain fatty acids and aromatic oils. Simplification of the two rejuvenators in molecular simulations leads to two structures, namely,

octadecadienoic acid ($C_{18}H_{32}O_2$) and small molecular aromatic ring ($C_{12}H_{16}$) [28, 29], as shown in Figure 3. The two structures are denoted as RE-1 and RE-2. RE-1 has a long-chain structure and a polar oxygen-containing functional group. RE-2 has an aromatic ring structure suitable for unraveling asphaltene agglomerate structures and has a small molecular weight. The admixtures of the two rejuvenators in aged asphalt are 3, 6, and 9 wt%. The corresponding numbers of molecules added are shown in Table 3.

3. Analysis of Microscopic Rejuvenation Mechanism and Rejuvenation Effect

3.1. Microscopic Rejuvenation Mechanism

3.1.1. Diffusion in the Contact Stage. Rejuvenator diffusion is the process of molecular movement from the high concentration of the rejuvenator fraction to the asphalt. During the mixing process between asphalt and rejuvenator, the rejuvenator molecules continue to move and begin to play a rejuvenating role. Therefore, the movement speed of the rejuvenator in the asphalt is an important factor affecting the size of the rejuvenator effect. The evaluation of this process is a key point that is difficult to achieve in practical experiments because the actual observation is biased toward a static description, and diffusion is a dynamic process [30]. With molecular simulations, molecular-level motions can be well predicted and summarized. In the simulation, the trajectories of the atoms in each model are recorded sequentially in accordance with time points. The distribution of the rejuvenator in the asphalt at different times can be clearly observed through the simulation. The contact of the rejuvenator with the asphalt can be determined in terms of the density change of the model. When the model density reaches the stabilization stage, the rejuvenator is in full contact with the asphalt and starts to work. The density curve is shown in Figure 4.

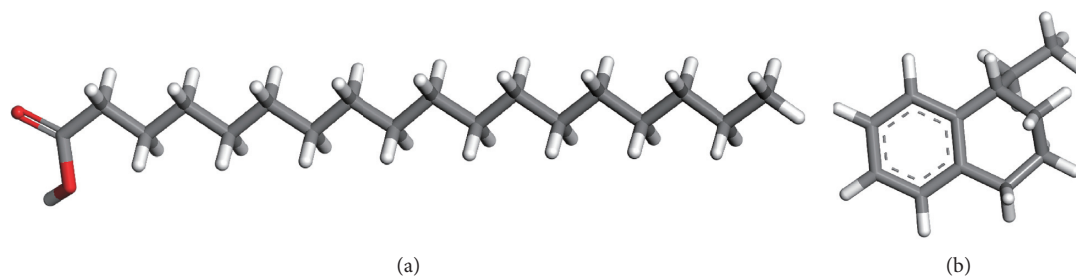


FIGURE 3: Molecular structure of two rejuvenators (left: octadecadienoic acid; right: small molecule aromatic ring).

TABLE 3: The amount of rejuvenator dosages corresponds to the number of molecules added.

Rejuvenator	Number of molecules		
	3 wt%	6 wt%	9 wt%
RE-1 (C ₁₈ H ₃₂ O ₂)	5	10	15
RE-2 (C ₁₂ H ₁₆)	9	18	27

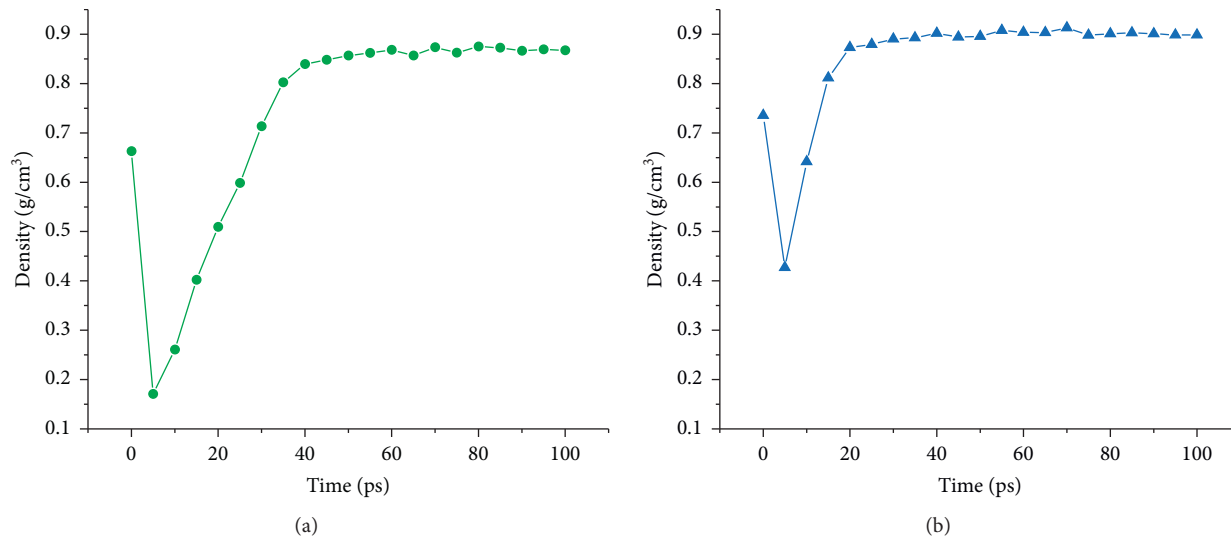


FIGURE 4: Density curve for diffusion model: (a) RE-1; (b) RE-2.

As shown in Figure 4, the two models reach the stabilization stage within 100 ps. The stable density is 0.867 and 0.898 g/cm³. RE-2 reaches the steady state faster than RE-1. The model was then placed in the NVT ensemble for 2 ns of free diffusion simulation. The degree of rejuvenator diffusion at 0, 2 ns time is shown in Figure 5.

As shown in Figure 5, the two rejuvenators have some degrees of diffusion after 2 ns of simulation. The red box line shows the intermixing part of the rejuvenator with the asphalt. The size of the intermingled fraction indicates that the molecules of the fraction in the aged asphalt diffuse further in RE-2. RE-2 diffuses more than RE-1. This condition is because the structure of RE-1 is different from the asphalt fraction and relies on the concentration to diffuse into the asphalt. Unlike RE-1, which has a long fatty chain, RE-2 has a smaller molecular weight and an aromatic ring structure. Therefore, RE-2, which is closer to the asphalt fraction, has a

better solubility to the asphalt; that is, RE-2 diffuses more strongly into the asphalt.

3.1.2. Diffusion in the Full Mixing Stage. When the rejuvenator is fully mixed in the asphalt, it can still move between the molecules of the asphalt fractions. The rejuvenator molecules are unaffected by the strong linkage of the asphalt fractions because diffusion is a physical process. Under thermal movement, the ability of the rejuvenator to move between molecules can reflect the magnitude of the subsequent rejuvenating effect. In the molecular simulation, mean square displacement (MSD) is used to describe the diffusion ability of the rejuvenator in asphalt. MSD is a measure of the average molecular displacement of molecules in the simulation. The formula is expressed as in the following equation:

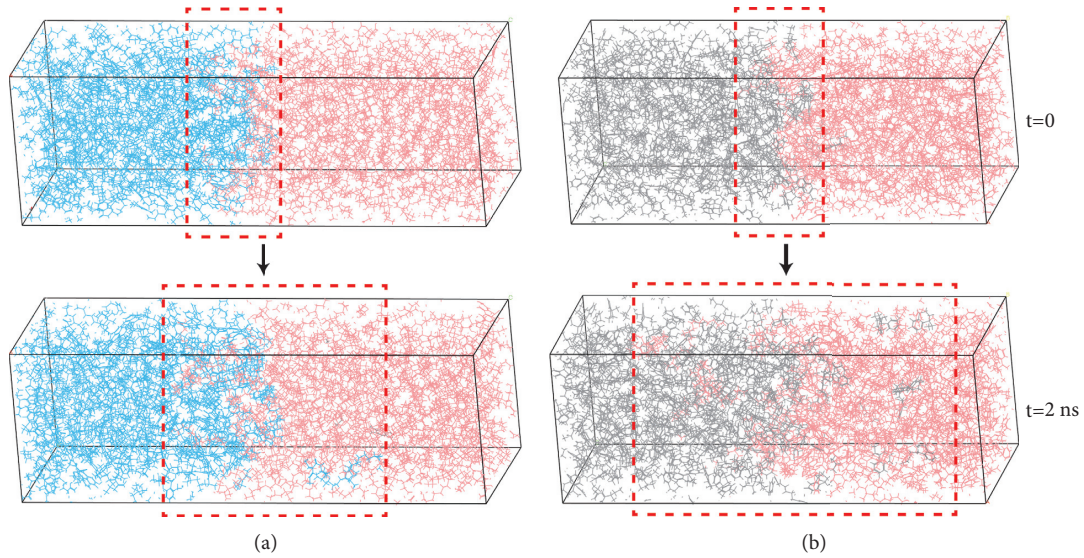


FIGURE 5: Different degrees of rejuvenator diffusion at 0, 2 ns: (a) RE-1; (b) RE-2 (red for aged asphalt, blue for RE-1, and gray for RE-2).

$$\text{MSD} = \left\langle |r_i(t) - r_i(0)| \right\rangle, \quad (2)$$

where $\langle \rangle$ is the average for all atoms in the group, r_i is the position vector of particle I , and 0 and t represent the initial moment and t moment. The MSD values of the model were calculated for the duration after running the optimized and stabilized model in the NVT ensemble for 500 ps. The system temperature was adjusted, and the MSD values were measured at 298 K. The calculation results are shown in Figure 6.

From Figure 6, the stable diffusion stage of rejuvenator molecules is in the range of 0–400 ps. The free movement stage of rejuvenator molecules is in the range of 400–500 ps. The stable stage is considered rather than the free motion stage of molecules due to its large variation. In the stabilization stage, the molecular mobility of RE-1 increases with the increase in dosage. By contrast, the mobility of RE-2 decreases with the increase in dosage. This finding shows that the diffusion characteristics of the two rejuvenators in the fully mixed stage are opposite. This condition is because the molecular structure of RE-1 has no aromatic ring structure and is less attracted by the asphalt fraction. RE-2 has an aromatic ring structure in its molecular structure and is more attracted by the large aromatic ring of the fraction. The long-chain structure of RE-1 is more entangled by the fraction molecules than the small molecule structure of RE-2. Therefore, the molecular mobility of RE-2 is reduced, indicating a lower diffusion ability.

3.1.3. Deagglomeration Effect. Asphaltenes in asphalt usually show self-aggregation behavior, and this aggregation increases with aging [31]. In this study, the RDF was used to evaluate the effect of two rejuvenators on the deagglomeration of asphaltene aggregation. The RDF can be used to describe the particle size distribution around the central atom. The calculation formula is shown in the following equation [32]:

$$g(r) = \lim_{dr \rightarrow 0} \frac{dN/4\pi r^2 dr}{\rho}, \quad (3)$$

where N is the total number of particles in the system, r is the distance from the reference particle to the central atom, and ρ is the number of particles per unit volume. When centered on asphaltenes, the aggregation behavior between asphaltenes can be evaluated. After a 500 ps dynamics simulation in NVT ensemble, the radius distribution of asphaltene pairs was analyzed. The results of the RDF calculation are shown in Figure 7.

As shown in Figure 7, aging shortens the accumulation distance between asphaltene pairs. And aged asphaltene pairs show a more regular peak arrangement than the virgin asphaltene pairs. This indicates that aging enhances the asphaltene aggregation effect. The distance between asphaltene pairs under the effect of RE-1 shows a trend of increasing and then decreasing. The opposite trend of decreasing and then increasing is found between asphaltene pairs under the action of RE-2. The effect of the two rejuvenators on the deagglomeration of asphaltene aggregation is opposite and is influenced by the amount of rejuvenator dosing. The two effects are most pronounced at 6%. At the dosage of 6%, RE-1 inhibits asphaltene aggregation, whereas RE-2 promotes asphaltene aggregation. The two rejuvenators show opposite effects at other dosing levels. This condition is because RE-2 has an aromatic ring type molecular structure, which is closely related to the deagglomeration of asphaltenes [29]. RE-1 does not have an aromatic ring structure, and its polar functional groups may not participate in aggregation or be detrimental to deagglomeration.

3.2. Microscopic Rejuvenation Effects

3.2.1. Viscosity. Viscosity is an important performance of asphalt. It affects the ease of construction and mixing and the high-temperature performance of asphalt in the visual

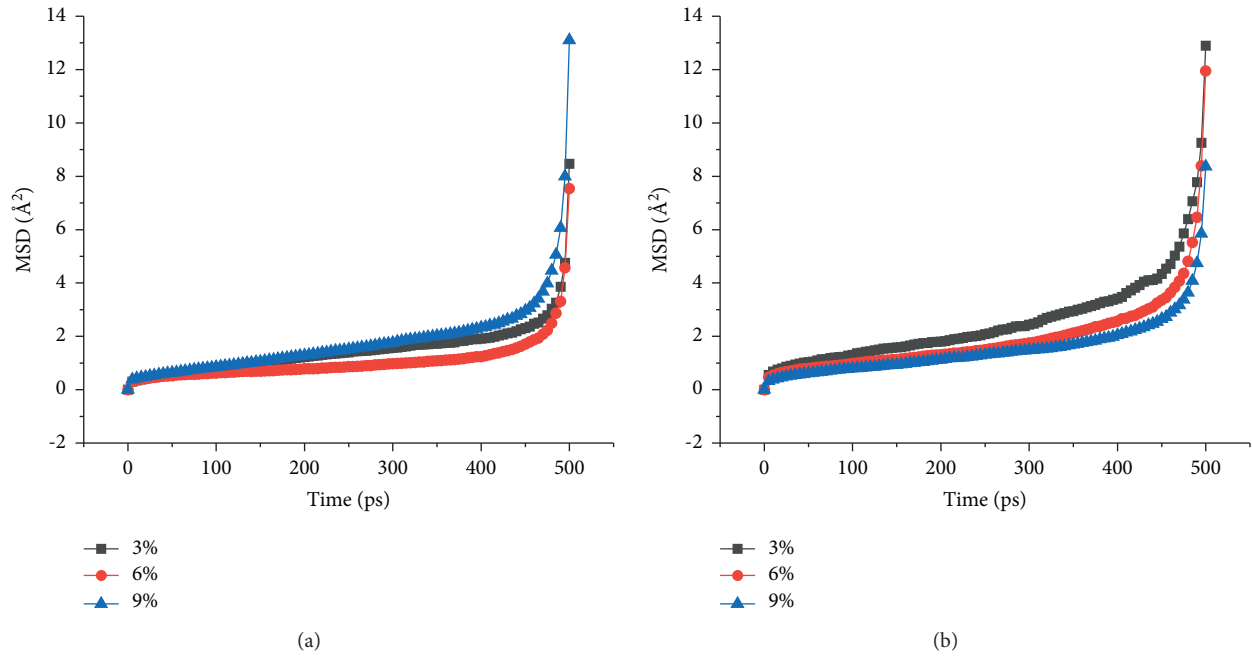


FIGURE 6: MSD values of the different dosages of rejuvenators at 298 K: (a) RE-1; (b) RE-2.

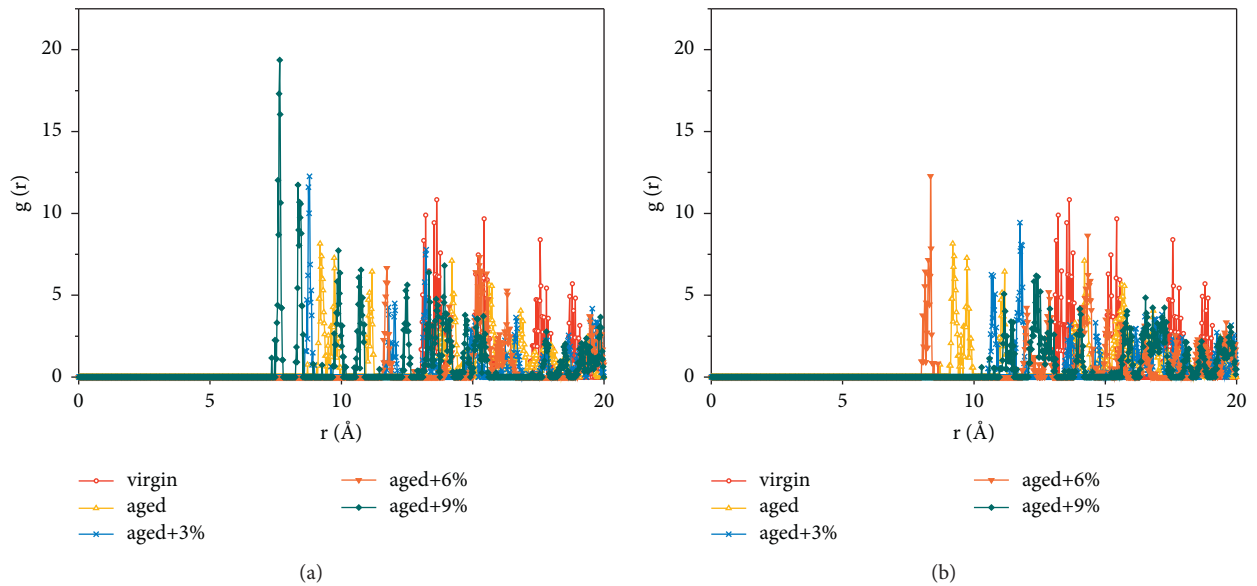


FIGURE 7: RDF curves of asphaltene pairs in aged asphalt under the effect of two rejuvenators: (a) RE-1; (b) RE-2.

representation [13]. High-viscosity asphalt is usually resistant to rutting, but the disadvantage is that it is difficult to mix [6]. Asphalt with low viscosity is easy to mix but has poor deformation resistance. Therefore, the extremely high or extremely low softening effect does not improve the performance when using rejuvenators to restore the viscosity of aged asphalt. The right amount of rejuvenator is the key to performance improvement. Practical tests usually have many viscosity testing methods that correspond to the macroscopic properties of asphalt. At the microscopic level of molecular simulation, viscosity can be considered the

structural strength of the molecule against shear [33]. This strength is characterized by the dynamic viscosity of the asphalt model at low-speed shear. The viscosities of bulk asphalt models were calculated using shear simulation in the Forcite module, which applied shear force to the model in one direction. In this study, the shear rate is 0.1 rpm. The set temperature is 298 K. The calculated results are shown in Figure 8.

From Figure 8(a), the viscosity of the asphalt model has a substantial increase after aging. The viscosity of the aged asphalt is reduced by up to 20% and 34% with the action of

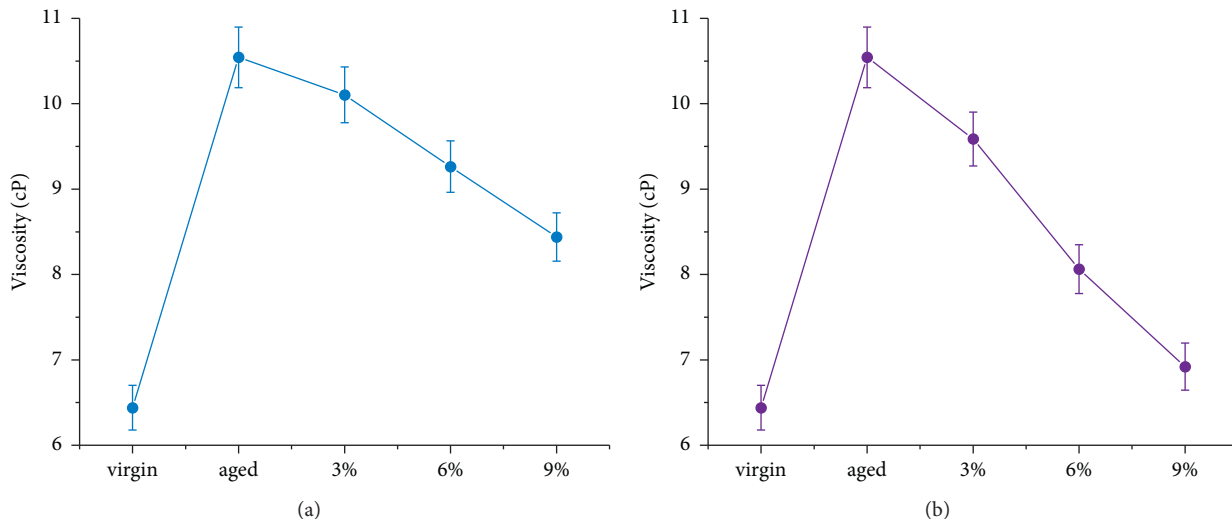


FIGURE 8: Viscosity change of virgin asphalt and aged asphalt with different rejuvenators: (a) RE-1; (b) RE-2.

the rejuvenator. RE-1 and RE-2 have a reducing effect on the viscosity of the aged asphalt. The softening effect of RE-2 is stronger than that of RE-1. The two rejuvenators have a better effect in softening the asphalt, and this effect increases with the increase in the admixture. This condition is because the molecular structure of the two rejuvenators is relatively simple, and the molecular weight is small, which does not produce a strong connection with the asphalt fraction. On the contrary, the rejuvenator can weaken the interaction between the fractions and is reflected in the reduction in viscosity of the asphalt.

3.2.2. CED. The compatibility of asphalt and rejuvenator is an important criterion to evaluate the performance of rejuvenator. The compatibility affects the stability of the rejuvenator in the asphalt and the overall stability of the asphalt [19]. This compatibility can be demonstrated in terms of the CED in the molecular simulation. All molecules in the asphalt model form stable connections with each other to generate strength, which is destroyed when a certain amount of energy is absorbed. When the absorbed energy is sufficiently large, the molecules return to an unconnected state. The CED is the amount of energy required to break all the connections per unit volume [34]. This value reflects the state of the asphalt model where stable joints are formed. When the difference between the values of the two models is large, the connections formed by the molecules of the asphalt fractions are unstable. Therefore, the CED difference between the rejuvenated asphalt and aged asphalt can be used to reflect the compatibility of aged asphalt with the rejuvenator. The formula for calculating CED is shown in the following equation:

$$\text{CED} = \frac{E_{\text{coh}}}{V}, \quad (4)$$

where $E_{\text{coh}} = E_{\text{intra}} - E_{\text{total}}$, which is the difference between the total energy within the molecule and the total energy of

the system, and V is the volume of the system. CED values were calculated by cohesive energy density simulation in the Forcite module. The calculation results are shown in Figure 9.

As shown in Figure 9, the two rejuvenators have a reducing effect on the CED. Aging increases the CED value of the virgin asphalt, indicating that oxidation strengthens the linkage of the fractions. The rejuvenator can weaken this linkage and restore it to the level of virgin asphalt. The weakening effect of RE-2 is stronger than that of RE-1. RE-1 gradually reduces the CED value of the aged asphalt close to that of the virgin asphalt, and the effect is no longer significant. RE-2 can always reduce the CED value of the aged asphalt. This condition indicates that RE-1 can restore the CED value of aged asphalt, whereas RE-2 can continuously reduce the CED value of aged asphalt. RE-2 weakens the internal connection force of aged asphalt and the internal connection force of virgin asphalt.

4. Discussion

The rejuvenation mechanism and rejuvenation effect of rejuvenators on asphalt were investigated by mixing two structures of rejuvenators with aged asphalt through molecular dynamics simulations. Molecular dynamics simulations have a great potential to be applied to asphalt. Some microscopic research methods beyond conventional tests can be realized to obtain more credible analytical and predictive results. The simulation results of this study show that the long-chain structure and oxidation functional groups of RE-1 make it have a different microscopic rejuvenation mechanism than the small aromatic ring structure of RE-2. Small aromatic ring rejuvenators can create π - π interactions with the polyaromatic ring structure of asphaltene. Thus, it is easier to produce strong interaction with asphaltene. This is the explanation for the improved compatibility of aromatic rejuvenators with asphalt. Long-chain rejuvenators rely on polar groups at the ends to create

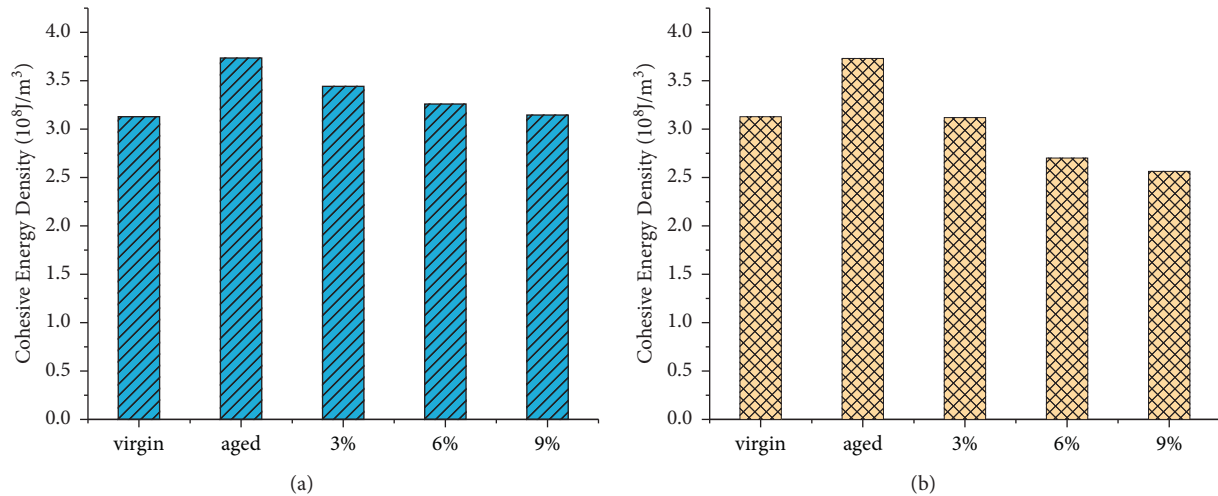


FIGURE 9: CED values of virgin asphalt and aged asphalt with different rejuvenators: (a) RE-1; (b) RE-2.

weak linkages with asphalt components. However, its most prominent role is to produce spatial obstruction utilizing long-chain structures or to reduce the strength of intermolecular connections. In the contact stage, the small molecules diffuse more easily than the long chains. The aromatic ring structure is an important factor in the mobility of the rejuvenator after sufficient mixing. The RDF curves confirm that the aromatic ring structure affects asphaltene aggregation. The degree of influence is determined in terms of the rejuvenator concentration. The selection of the right concentration in the addition has a more effective effect on the asphaltene aggregation. The results of viscosity and cohesion density illustrate the rejuvenating effect of two rejuvenators. RE-2 has a more significant rejuvenating effect than RE-1 and recovers the properties of aged asphalt quickly.

In practical applications, the rejuvenators are used to contain more complex structures [35]. Rational control of the number of aromatic ring structures, long-chain structures, oxidation functional groups, and molecular weight are important concerns influencing the performance of the rejuvenators. The study of asphalt and rejuvenator through molecular dynamics simulation is a good prospect to achieve the optimal selection of rejuvenator. With the development of computational software, conducting simulations of complex structure combinations that are suitable for the actual rejuvenator ratios is recommended.

5. Conclusion

In this study, molecular dynamics simulations were used to investigate the microscopic rejuvenation mechanism and rejuvenation effects of rejuvenators in aged asphalt. This mechanism is reflected by the diffusion characteristics and deagglomeration of the rejuvenator in asphalt. The change in viscosity, CED, and density reflects the rejuvenation effect.

- (1) The analysis of the diffusion characteristics of the rejuvenator in contact with asphalt shows that the small molecule structure is more favorable than the

long-chain structure to promote the initial dissolution diffusion. After full mixing with asphalt, the rejuvenator containing aromatic ring structure is attracted to reduce the diffusion, whereas the oxidation functional group structure is unaffected.

- (2) The RDF curves show that the two rejuvenators have the most specific action effect at 6 wt% dosage. Overall, the aromatic ring structure similar to that of asphaltene has a significant effect on agglomeration.
- (3) The rejuvenation of asphalt is influenced by the diffusion ability and the disaggregation ability of the rejuvenator. Appropriate RE-1 and RE-2 contents can ensure the diffusion and deagglomeration of asphaltene aggregation at different stages.
- (4) Molecular simulations of the rejuvenation effect show that RE-1 and RE-2 reduce the viscosity of aged asphalt by up to 20% and 34%, respectively. The long-chain structure has a better softening ability for aged asphalt than the aromatic ring structure.
- (5) The CED results indicate that RE-1 helps maintain the intermolecular compatibility of asphalt more than RE-2. RE-1 can restore the aging to its virgin level, and RE-2 can further continue to reduce the CED value.

Data Availability

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

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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