Research Based on the Selection of Regenerative Agents Based on Molecular Simulation New-Old Asphalt Diffusion Behavior

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Abstract. In order to understand the new-old asphalt diffusion behavior, use the Materials Studio (MS) molecular dynamic simulation software to build a matrix asphalt and aging asphalt molecular model based on the average molecular model of the asphalt, and select the appropriate force field and potential energy function. As well as parameters such as boundary conditions, set up asphalt-regenerative dot-shaped contact models and laminar contact models. From the perspective of molecular perspectives, the diffusion behavior between the old and new asphalt and the regenerative agent is analyzed. The promotion effect of the asphalt diffusion behavior, the simulation results show that the asphalt's internal diffusion process is mutual, and the promotion effect of aromatherapy regeneratives on the spread of new and old asphalt under the same conditions is better than chain regenerative agents and waste oil regeneration agents.

1 INTRODUCTION

Asphalt is one of the commonly used materials in road construction and maintenance, and over time, asphalt undergoes internal structural changes and its properties change under the effect of high temperatures over a long period of time, i.e., asphalt aging. In road construction and maintenance, asphalt recycling technology can not only solve the problem of environmental pollution and waste resources, but also significantly reduce the cost of road construction [1][2][3].

With the premise that the demand for recycled asphalt mixture obtained from RAP (Recycled Asphalt Pavement) is increasing in actual projects, studying the mechanism of asphalt regeneration from a microscopic perspective can provide a better understanding of the influence of various factors in the process of asphalt regeneration. It is necessary to analyze and study the diffusion state of the regenerant on the surface of aged asphalt in the actual use process, and apply the corresponding force field parameters through molecular dynamics software to obtain the molecular dynamics in-formation, and then reproduce the intermolecular forces to clarify the asphalt aging mechanism and provide the theoretical basis for the optimal selection of regenerant.

It was shown [4] that the internal structure of asphalt is complex and it contains hundreds of molecular types, and nowadays it is not clear that all the molecular species inside it, and the wide range of molecular structures cannot be simulated and calculated one by one in a computer. The first study to establish the molecular model of asphalt was proposed by Dickie et al [5] in 1967 to replace the asphaltene molecule with the Yen structure model. Mullins O C et al [6] proposed three molecular structures of asphaltene to represent the asphalt model based on the asphaltene based molecular model, which can reflect the molecular structure of asphaltene more realistically. Li and Greenfield [7] proposed a structural molecular model of 12 molecules to represent the structures of different components within asphalt based on the extraction of the structures of four components: gum, aromatic fraction, saturated fraction and asphaltene. It was shown that the 12 structural molecular models constructed in this way can reflect the structure and properties of asphalt more realistically and provide a more accurate model for research in the field of asphalt. Rogel et al [8] used molecular dynamics software to construct an average molecular model of asphaltene, which simulated the structure and motion of asphaltene molecules, allowing the molecular structure of asphaltene to be presented more clearly. Paull et al [9] designed asphalt-related performance tests to verify the accuracy of the single-molecule model of asphalt developed by Jenning [10], and compared the model results with experimental data for analysis, which showed that the model could more accurately simulate the real properties and behaviors of asphalt materials, providing a very effective tool for studying the properties and behaviors of asphalt.

In addition, many scholars [11][12] studied the internal structural changes of molecules by establishing a molecular model of asphalt, and then analyzed the diffusion behavior of the regenerant within the aging asphalt. Sun et al [13] analyzed the self-healing ability of asphalt from the...
microscopic level by calculating the density, concentration, and displacement of asphalt through molecular simulation, and the results showed that the molecular movement process within asphalt is influenced by temperature, and the higher the temperature, the higher the temperature, the greater the self-healing property. Ding [14] used molecular dynamics simulation (MD) to build a three-component model based on asphaltenes, resin, and oil, and analyzed the internal spatial movement of asphalt by calculating the radial distribution function of each molecule in the asphalt. The study found that the molecular movement of asphalt can play a key role in the diffusion process of old and new asphalt, and the addition of regenerating agent can promote the degree of miscibility of old and new asphalt.

To this end, this study starts from the nature of asphalt, through in-depth research on the key mechanisms of molecular structure changes, chemical reactions and the separation and reorganization of asphalt components during asphalt regeneration process, the molecular dynamics software is used to establish the average molecular model and the model of different components of the regenerant, and the asphalt-regenerant laminar contact model is constructed according to the type of regenerant, and the diffusion behavior of different regenerants on the surface of old asphalt is analyzed To preferably select the regenerating agent to better guide the preparation process of recycled asphalt and improve its quality and performance.

2 MODEL BUILDING

2.1 Molecular modeling

Asphalt is a mixture of polymeric organic compounds and non-metallic elements, and its main components are hydrocarbons, including aliphatic and cycloalkanes, which have a wide variety of internal molecules and complex internal system structure, so it is difficult to establish a complete molecular model of asphalt from the microscopic level. At present, many researchers have analyzed and improved the establishment of asphalt molecular model, trying to use the average molecular model to describe the asphalt expansion and healing process from the molecular point of view, and the results obtained are approximately the same as the real chemical composition of asphalt, with a better simulation effect.

In this study, based on the existing results, the average molecular structure model of asphalt from Sun [13] was chosen as the matrix asphalt for the study, whose molecular formula is C75H104OS, and the main products of asphalt aging were added to the oxidation-prone positions in the matrix asphalt, thus simulating the chemical change process of aging asphalt. The molecular models of matrix asphalt and aging asphalt are shown in Fig.1 and Fig.2.

Where white indicates hydrogen atoms; gray indicates carbon atoms; red indicates oxygen atoms; and yellow indicates sulfur atoms, hereinafter.

In this study, based on molecular dynamics simulation, the microscopic behavioral changes of three different regenerants, aromatic, waste oil and chain, in the old asphalt and the degree of miscibility of the old and new asphalt were studied by constructing three single-component regenerants to provide a microscopic information basis for selecting a better regenerant. As shown in Fig.3, Fig.4 and Fig.5.

During the simulation, the NPT and NVT systems were selected to relax each system, and the COMPASS force field was applied, where the truncation radius of the non-bonding and van der Waals forces was 18.5 Å. The temperature was controlled by the Nose-Hoover method, and the temperature was set to 298 K. The pressure was controlled by the Andersen method at 0.0001 GPa, and the
The simulation step was 1 fs; the total simulation time was 100 ps. The total simulation time was 100 ps.

The optimized molecular model has the minimum energy and reaches the equilibrium state, and the molecular model in this state will not be erroneous due to the long convergence time.

To verify the validity of the asphalt model, the density of the asphalt model at the set temperature is calculated after a certain length of simulation for a given system synthesis. By comparing the results calculated from the simulations with the known experimental data, conclusions can be drawn as to whether the model assumptions are valid, whether the parameter settings are reasonable, and whether the results are as expected, thus providing favorable conditions for subsequent simulations.

The density values obtained from the simulations for the matrix asphalt as well as the aging asphalt vary as shown in Figure 6.

![Figure 6 Asphalt density variation](image)

It can be seen that the density of matrix asphalt gradually becomes larger with the time step, when the step is 100 ps, the density value tends to 1.02 g/cm³, but the density value of aging asphalt is slightly larger than that of matrix asphalt, and its density value tends to 1.06 g/cm³ after stabilization, and the density value after stabilization is shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Substrate asphalt (g/cm³)</th>
<th>Aging asphalt (g/cm³)</th>
<th>Available data 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>298K</td>
<td>1.02</td>
<td>1.06</td>
<td>1.01~1.04</td>
</tr>
</tbody>
</table>

In comparison with the existing experimental data, it was found that the density values of matrix asphalt and aged asphalt obtained by using the average molecular model simulation were basically the same as those obtained from the experimental asphalt, in which the reason for the large density values of aged asphalt obtained from the software simulation may be that the molecular simulation software has a more ideal environment, ignoring the results of the large density values caused by the reduction of light components in the aging process of the actual asphalt.

### 2.2 Contact modeling

The establishment of asphalt molecular model is the first step to simulate the fusion process of old and new asphalt, while the complex miscibility process between old and new asphalt molecules also requires the use of molecular dynamics means to further simulate the molecular motion pattern inside the structure from the atomic perspective, by constructing asphalt contact model and introducing diffusion coefficient to evaluate the diffusion behavior, in order to observe the diffusion behavior of the regenerant on the surface of old asphalt and the degree of fusion of old and new asphalt on this basis, to provide a theoretical basis for the optimal selection of regenerant. As shown in Figure 7 and Figure 8.
The green color indicates aromatic regenerant, the yellow color indicates waste oil regenerant, and the purple color indicates chain regenerant, the same below.

The laminar contact model of the regenerant mainly consists of matrix asphalt, aged asphalt and regenerant, which can further observe the internal molecular motion of the old and new asphalt or old and new asphalt-regenerant, and quantitatively evaluate the degree of integration of the old and new asphalt through the establishment of the model and the comparison of each parameter. As shown in Figure 9, Figure 10 and Figure 11.

The constructed laminar contact model should be relaxed to reach the equilibrium state, and the stable model should be put into a unified system for analysis. According to the force field, time step and calculation parameters determined in the previous paper, a suitable evaluation method and index should be selected to conduct a comprehensive and systematic analysis and study of the regenerant diffusion process in the light of the actual application.

Based on the structure of the molecular model constructed in the previous paper, the structure of each molecule is optimized, and the geometry of the laminar contact model is optimized by using the geometry optimization command in the Forcite module of MS software. In order to make the model close to the real situation, the system should be simulated with a constant volume and temperature, and the unstable molecules in the structure should be eliminated, so that the obtained molecular system can reach the energy minimization.

The molecular parameters, chemical composition and concentration are the internal factors that influence the diffusion between the old and new asphalt and the regenerant, in addition to the external temperature, which is an important influence. Therefore, in addition to the effect of the regenerant on the degree of integration of the old and new asphalt, the effect of different temperatures on the diffusion and miscibility of the old and new asphalt should be considered. By setting three different temperature types for NPT equilibrium at a standard atmospheric pressure: 298 K (25°C), 333 K (60°C), and 433 K (160°C), and other simulation parameters were set as before.

3 EVALUATION INDICATORS

3.1 Mean square displacement

During the diffusion simulation, the molecules in the system are nested in each other and finally reach the equilibrium state. The Mean Square Displacement (MSD) can reflect the ability to transfer heat and information in the system, and further monitor the diffusion process in the system.

To study the diffusion behavior of different regenerants within the asphalt at 298 K. According to the asphalt-regenerant laminar contact model constructed in the previous paper, the system equilibrium was reached by running 100 ps under the NPT system synthesis, and then the analysis command under the Forcite module was used to analyze the particle motion process and obtain the mean square displacement curve to obtain the MSD curve changes corresponding to the three regenerants at 298 K. As shown in Figure 12.

It is known that the slope of the mean square displacement-time relationship plot is correlated with the diffusion coefficient, i.e., the degree of change of the MSD curve can reflect the molecular diffusion rate. From the figure, it can be seen that the change curves of MSD in the three final models all show an increasing trend and smooth changes, which indicates to some extent that the constructed models have a certain degree of mobility.

Since the diffusion behavior in the simulation process is random, the diffusion behavior is analyzed according to the image change curve: when the running time is in the stage of 0–20ps, the aging asphalt fills the void rapidly after contacting with the regenerant, which makes the slope of the curve in the early stage larger due to the rapid and irregular movement of particles in the system; after 20ps,
the molecules in the system keep diffusing into the internal filling microscopic void and gradually reach a relatively stable state. After 20 ps, the slope of the curve also stabilizes, and the relationship between the mean square displacement and time can be seen as a linear positive correlation. The motion process is consistent with the equilibrium state in the molecular simulation process, and a side by side comparison of the MSD values of the three regenerants shows that the diffusion effect of aromatic regenerants and waste oil regenerants is better than that of chain regenerants.

Temperature is the main reason affecting the diffusion rate of the regenerant in the aged asphalt. Therefore, molecular dynamics simulations were conducted for different regenerant models to consider their diffusion rates in the aged asphalt at 298 K, 333 K and 444 K. Taking the aromatic regenerant as an example, the MSD variation curves were plotted as shown in Figure 13.

![Figure 13 MSD variation curves of aromatic regenerants at different temperatures](image)

It is obvious from the figure that the MSD value increases with the increase of temperature. From the perspective of molecular thermal motion, this is due to the increase in temperature in the system, which further increases the kinetic energy and promotes the intermolecular diffusion, resulting in the gradual increase of MSD value. In addition, the increase of temperature will reduce the viscosity of asphalt and rejuvenator, and the reduction of viscosity is also beneficial to the mutual diffusion in the system. The high temperature will cause the regenerant to volatilize, which is not conducive to the diffusion behavior, so the diffusion behavior continues with the increase of temperature, but the diffusion rate is gradually slowed down by the temperature.

### 3.2 Diffusion coefficient

The diffusion coefficient is a more direct reflection of the relative rate of diffusion of the substance, which is calculated by the relationship between the mean square displacement and time.

\[ D = \lim_{t \to \infty} \frac{1}{6t} \frac{\text{MSD}(t)}{k} \]

where \( D \) is the diffusion coefficient; \( t \) is time; and \( k \) is the slope of the mean square displacement-time curve.

The diffusion coefficients of different regenerants at 298 K, 333 K and 433 K were calculated according to equation (1) as shown in Table 2 below.

### 4 RESULTS AND DISCUSSION

(1) The contact model simulation results show that at a certain temperature, the diffusion coefficient is significantly improved in the two-layer model with the addition of regenerant compared with the old and new asphalt models without the addition of regenerant, indicating that the addition of regenerant can improve the migration rate of molecules within the asphalt; the addition of aromatic regenerant has a more significant effect on the increase of diffusion coefficient than the addition of waste oil regenerant and chain regenerant, i.e., the promotion effect (2) For either of the two-layer models, the aromatic rejuvenator > waste oil rejuvenator > chain rejuvenator.

(2) For either two-layer model, the increase in temperature has a significant effect on the diffusion of the regenerant in the aged asphalt and the mutual diffusion of the matrix asphalt and the aged asphalt, and it can be tentatively concluded that the in-crease in temperature can promote the molecular movement in the system. With the increase of temperature in the system, the addition of regenerant can promote the molecular migration rate in the system, and the promotion effect of aromatic regenerant is significant.

(3) In this paper, Materials Studio was used to verify the good diffusion ability of aromatic regenerants in asphalt, which indicates that the molecular dynamics simulation of the diffusion behavior of regenerantaged asphalt is reliable.

### REFERENCES


