Molecular Dynamics Study on the Compatibility of Asphalt and Rubber Powder with Different Component Contents

Mingxing Gao, Yaolu Chen, Conghao Fan, and Meijian Li

ABSTRACT: In order to study the influence of asphalt from different origins on the compatibility of rubber powder and asphalt, the four most representative 90# asphalts from different origins were selected for the four-component test, namely, Karamay, Shell, Esso, and HuanxiLing, which have differences in their micro-structure and molecular structure. First, Materials Studio software was used to build the asphalt molecular model based on the four-component test data, and styrene butadiene rubber and natural rubber were used as representative molecules of rubber powder to build the molecular model. The solubility parameters, molecular potential energy, and radial distribution function were obtained by molecular dynamics simulation of rubber powder and four asphalt molecules. The gray correlation degree analysis of the four components of asphalt is carried out with the gray correlation method. The results show that the solubility parameter difference between Esso asphalt and the rubber molecule is the smallest, and the potential energy between them is the largest; that is, the compatibility between Esso asphalt and rubber powder is the best, followed by Shell, HuanxiLing, and Karamay. The analysis of the radial distribution function between two molecules also further confirmed the compatibility of the four modified asphalt. The gray correlation degree between the four components of asphalt and the solubility and molecular potential energy index is as follows: saturates > aromatics > resin > asphaltene. It is concluded that the influence of light components on the compatibility of asphalt is greater than that of heavy components. Therefore, in future industrial production, the rubber powder-modified asphalt made of more light components has better performance and storage stability.

INTRODUCTION

According to global database statistics, the world produces 1.5 billion tires every year, equivalent to 17 million tons of waste tires. Improper handling of old tires will cause great harm to the environment. Adding waste tire rubber powder into asphalt to prepare rubber powder-modified asphalt can not only solve the problem of environmental pollution but also improve the performance of asphalt. Compared with base asphalt, rubber powder-modified asphalt has better stability at a high temperature, crack resistance at a low temperature, temperature sensitivity, and aging resistance. However, the difference in the molecular structure between rubber powder and asphalt will directly affect their compatibility, which will affect the service performance and storage stability of modified asphalt. Therefore, compatibility is the primary problem to be solved in the research of rubber powder-modified asphalt. The compatibility of modified asphalt has been studied by some scholars. At the macro level, some scholars choose to improve the compatibility of rubber powder-modified asphalt by adding compatibilizers. For example, Liang et al. proposed that trans polyoctylamine could improve the compatibility and storage stability of rubber powder-modified asphalt. Liu et al., through image analysis, proposed that grass and wood ash by-products as adhesion promoters can greatly improve the adhesion performance of modified asphalt. Fini et al. used bio-binder as an additive of the rubber powder-modified asphalt binder to improve compatibility and reduce segregation while enhancing its stability. Xu et al. provided rubber-modified asphalt with higher compatibility by adding waste oil and microwave desulfurization. However, the main problem faced by this part of the research is that the adhesive with a high effect is often expensive, and it will increase the consumption of funds in the deployment of rubber-modified asphalt, which is not conducive to the actual construction. Therefore, some scholars choose to adjust the blending ratio of the admixture in modified asphalt.
asphalt to achieve higher compatibility. For example, Jitsangiam et al. investigated the influence of natural rubber (NR) latex content on the performance of the rubber-modified asphalt binder and found that when NRL content was 7%, there was cross-linking and bridging between NRL and the original asphalt binder, and the optimal mix ratio of the rubber-modified asphalt binder was finally obtained.\(^{11}\) Xin et al. evaluated the stability of rubber asphalt by adjusting ore powder content and using rut tests at different temperatures.\(^ {22}\) However, the optimal mix proportion of different kinds of asphalt raw materials and rubber powder is different, which has a certain impact on the actual construction. It can be seen that there are certain limitations to improving the compatibility of rubber-modified asphalt from the macro level, and it is necessary to further explore the micro components of asphalt.

At the micro level, molecular dynamics (MD), as a new powerful numerical tool, can help to understand the basic mechanical relations of asphalt concrete at the atomic scale. Therefore, MD can be used as a suitable tool to predict the properties of asphalt materials and discuss the macroscopic properties and microscopic behavior.\(^ {13}\) In recent years, more and more researchers have used MD to study the microscopic properties of asphalt.\(^ {14,15}\) Based on the four-component theory, molecular models of representative asphaltenes were constructed to study the self-healing properties of asphaltenes, the nano-structure of the asphaltene and aggregate interface, the adhesion properties of asphaltenes and aggregates, and the effects of oxidative aging on asphalt properties.\(^ {16}\) Xu et al. established the MD model of the asphalt diffusion system and obtained that the increase in temperature was conducive to the diffusion of asphalt on the surface of the aggregate and promoted the adhesion between the asphalt and aggregate.\(^ {17}\) Xu et al. developed an atomic simulation framework and finally concluded that the water content between the asphalt and aggregate interface would reduce the bonding strength of the interface.\(^ {17}\) The above studies mainly focus on the influence of temperature, moisture content, and other external factors on the compatibility between the asphalt and aggregate, while ignoring the influence of asphalt components on the compatibility of rubber asphalt. There are some differences in the molecular components of asphalt from different origins, so the main purpose of this study is to explore the influence of different molecular components of asphalt on the compatibility of rubber-modified asphalt.

In this paper, the molecular models of four asphalts and one rubber are established. Using the MD simulation method, solubility parameters, interaction energy, and radial distribution function as characterization parameters, combined with the gray correlation method, the influence of different asphalt component contents on the compatibility of asphalt powder and asphalt was studied. It provides a theoretical basis for the research and development of rubber-modified asphalt.

### MATERIALS AND METHODS

**Asphalt Molecular Model.** Bitumen is a mixture mainly derived from the distillation of crude oil and consists of a variety of (predicted million) organic compounds. According to the four-component theory, asphalt can be divided into four components: asphaltene, colloid, aromatic, and saturated. Gunay et al. studied the rheological properties of different types of asphalt binders and compared their composition and physical properties. Through NMR tests, they found that asphaltenes contained an aromatic ring group and some short-branched chains.\(^ {18}\) Maity et al. treated natural asphalt with modifiers, and the number of aromatic sheets was increased. The double bond and the COOR functional group of C\(_{18}\) acrylates could promote the polymerization reaction between modifiers and natural asphalt. NMR analysis of bitumen shows that the molecular chain length of bitumen alkanes is distributed between C\(_{16}\) and C\(_{50}\) and C\(_{22}\) is located in the middle part of this interval.\(^ {19}\) Ren et al. studied the density difference between polymer and asphalt components caused by the deposit stability problem, established the polycyclic aromatic hydrocarbons in alicyclic hydrocarbons as basic structures with different lengths of the alkyl carbon chain containing sulfur, nitrogen, oxygen, other impurity atoms, and the corresponding groups of gelatin molecules model, which this paper adopts on behalf of gelatin molecules.\(^ {20}\) Xu et al. pointed out that the alkane C\(_{32}\)H\(_{64}\) contained in asphalt has the highest content, and the softening point and boiling point of C\(_{32}\)H\(_{64}\) are consistent with the softening point and boiling point of most asphalt oils. Therefore, dodecane C\(_{32}\)H\(_{64}\) was selected as the representative molecular model of saturation fraction. The structure of aromatic molecules is similar to that of 1, 7-dimethylnaphthalene, and the number of aromatic rings and branched chains contained in the molecules are suitable for oil and asphaltene intermediates.\(^ {21}\) Ren et al. believe that the basic structure of asphaltenes is a thick and aromatic ring system composed of multiple aromatic rings as the core, surrounded by a number of naphthenic rings. Both aromatic rings and naphthenic rings contain a number of normal alkyl side chains with different lengths, which contain various groups containing sulfur, nitrogen, and oxygen.\(^ {22}\) In summary, the asphalt four-component model constructed using Materials Studio is shown in Figure 1.

![Figure 1. Asphalt molecules consist of these four components: (a) asphaltene; (b) resin; (c) saturates; (d) aromatics.](https://doi.org/10.1021/acsomega.2c02813)

In order to study the effect of asphalt component content on the compatibility of rubber powder and asphalt, four kinds of 90# asphalts of Karamay, Shell, Esso, and HuanXilIng were selected, which were recorded as no. 1, 2, 3, and 4, respectively. According to the test method of T0618-1993 in JTJG E20-2011 “Testing Procedures for Asphalt and Asphalt Mixtures for Highway Engineering”, four kinds of asphalts were analyzed by four components. The experimental data are shown in Table 1.

The molecular model of the matrix asphalt was constructed according to the ratio in Table 1 using the amorphous cell module in the MS; asphalt model parameters are shown in Table 2. Taking the Karamay 90# asphalt as an example, as shown in Figure 2.

**Rubber Powder Molecular Model.** NR and styrene–butadiene rubber (SBR) are the main components in rubber...
powder, which affect the performance of rubber powder-modified asphalt. Therefore, the NR model and SBR model were used to construct the rubber molecular model. NR is a homopolymer formed by the polymerization of monomers, and the molecular chain structure can be constructed by specifying the number of repeating units. SBR is a random copolymer composed of styrene and butadiene monomer polymerization, mainly prepared by styrene and butadiene emulsion polymerization. The content of styrene in SBR is about 23.5%, and that of butadiene is about 76.5%. Butadiene is composed of 76% trans-1,4-butadiene, 7% cis-1,4-butadiene, 16% 1,2-butadiene, and 1% of other substances.

Based on the above data, the random copolymer function of MS software was used to construct the NR and SBR single-chain models with a chain length of 50, as shown in Figure 3. Four NR and SBR single-chain molecules are selected, and a rubber powder molecule is constructed through the amorphous cell module, as shown in Figure 4.

**MD Calculation.** Due to the high energy and unreasonable structure of the initially constructed molecular model of asphalt and rubber powder, geometric structure optimization and MD optimization are required to keep the model in a stable structure with low energy, so as to make the model closer to the real state. The geometric structure of the model was optimized under the COMPASS force field, and then a simulated annealing treatment was carried out for five cycles between 300k and 500k to eliminate unreasonable conformation. The first dynamic simulation of the molecular model was carried out under 298 K constant temperature and pressure ensemble (NPT). The number of steps was set to 100,000, the total duration was 100 ps, and one conformation was output every 1000 steps. The last stable conformation was selected for the second dynamic simulation under the 298 K regular ensemble (NVT). The number of steps was set to 100,000, the total duration was 100 ps, and one conformation was output every 1000 steps. The diagram of energy variation with time is obtained, as shown in Figure 5.

As can be seen from Figure 5, after 200 ps of MD simulation, the energy fluctuation of each system is small and tends to the equilibrium state. Due to the high content of asphaltenes and colloid in macromolecules in asphalt no. 1, the molar mass of asphalt molecules is relatively large. According to the mass and energy equation, the higher the molar mass is, the higher the energy is.

Asphalt density is an index of the molecular density of asphalt and also an index of asphalt quality performance, which is closely related to its physical properties and chemical composition. In order to verify the accuracy of the molecular model, the density of the molecular model at 25 °C was selected as the comparison index, which was compared with the density of the real asphalt (1.02 g/cm³) and the real rubber (1.18 g/cm³). The results are shown in Table 3.

Asphalt and rubber powder are a complex polymer mixture, and its molecular model is the representative molecular model of each component, which is different from the real material. It can be seen from Table 3 that the difference between the model density and the real density is within 10%. Combined with the changes in molecular energy and density, it can be determined that the molecular model of asphalt and rubber powder can represent the real material structure.

**MD Simulation of the Asphalt and Rubber Powder Mixture.** Use MS software in the amorphous cell module construction of the asphalt and rubber powder blending system. Generally speaking, the optimal content of rubber powder-

| number | sample   | size               | number of atoms |
|--------|----------|--------------------|-----------------|
| 1      | Karamay  | 34.183 Å × 34.183 Å × 34.183 Å | 4321             |
| 2      | Shell    | 34.183 Å × 34.183 Å × 34.183 Å | 4259             |
| 3      | Esso     | 34.183 Å × 34.183 Å × 34.183 Å | 4111             |
| 4      | HuanXiLing | 34.183 Å × 34.183 Å × 34.183 Å | 4233             |

Table 1. Asphalt Four-Component Ratio

| number | sample | As | S | Ar | R   |
|--------|--------|----|---|----|-----|
| 1      | Karamay| 3.0| 38.57| 22.47| 35.96 |
| 2      | Shell  | 7.42| 54.16| 25.54| 12.88 |
| 3      | Esso   | 10.86| 32.87| 51.2| 5.07 |
| 4      | HuanXiLing | 12.16| 41.44| 22.23| 24.17 |

Table 2. Asphalt Model Parameters

Figure 2. Karamay asphalt molecular model.

Figure 3. Rubber molecular model is composed of the (a) molecular model of NR and (b) molecular model of SBR.

Figure 4. Molecular model of rubber.
modified asphalt is about 20%, so the rubber powder content selected in this paper is 20%. MD simulation of the asphalt and rubber powder blending system was carried out. The NVT regular system was used in fully mechanized mining. The temperature was 160 °C, the number of steps was set as 100,000 steps, and the total duration was 100 ps. The solubility parameters and interaction energies of the blends can be calculated.

■ RESULTS AND DISCUSSION

Solubility Parameter. The solubility parameter is an important thermodynamic parameter to represent the properties of polymer solution. Its physical meaning is the square root of cohesive energy density.

\[ \delta = \sqrt[3]{\frac{E}{V}} \]  

(1)

E represents the cohesive energy of the copolymer; V represents the molar volume; and E/V represents the cohesive energy density.

The free energy variation in the mixing process determines the compatibility degree of the two polymers. If \( \Delta G_m < 0 \), which indicates that two kinds of polymer can be fully compatible to form a homogeneous system.

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

(2)

\( \Delta G_m, \Delta H_m, \) and \( \Delta S_m \) represent the free energy, mix in the process of mixing enthalpy, and entropy of mixing, respectively.

In terms of capacitive mixing of polymers, the mixing process is always endothermic, namely \( \Delta H_m > 0 \), which means that the enthalpy of mixing always hinders the compatibility of copolymers.

\[ \Delta H_m = \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2 V \]  

(3)

\( \varphi_1 \) and \( \varphi_2 \) represent the volume fraction of copolymers 1 and 2, respectively.

In order for the polymer to have good compatibility, it is inevitable that the \( \Delta H_m \) is as small as possible, which requires the solubility parameters of the two copolymers to be similar.

After calculation by MD, the cohesive energy density and solubility parameters of the four asphalt molecules and rubber molecules were obtained, as shown in Table 4.

| sample   | density (g/cm³) | error (%) |
|----------|----------------|-----------|
| asphalt 1| 0.991          | 2.84      |
| asphalt 2| 0.977          | 4.22      |
| asphalt 3| 0.943          | 7.55      |
| asphalt 4| 0.971          | 4.80      |
| rubber   | 1.07           | 9.32      |

Table 3. Molecular Model Simulation Density vs Actual Density

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

It can be seen from Table 4 that the difference in solubility parameters of the four kinds of asphalt and rubber powder is less than 4.10 (J cm⁻³)¹/², which verifies the rationality of the molecular model. Among them, the solubility parameter difference between no. 1 asphalt and rubber powder is the largest, and the solubility parameter difference between no. 3 asphalt and rubber powder is the largest because the content of asphaltene and resin in no. 1 asphalt is higher than that of no. 3 asphalt. According to the compatibility principle, the greater the difference in free energy between two polymers, the more

Figure 5. Molecular potential energy of rubber powder.

Table 4. Cohesive Energy Density and Solubility Parameters of Four Kinds of Asphalt and Rubber Powder

| sample   | CED/(J m⁻³) | \( \delta / (J \text{ cm}^{-3})^{1/2} \) | \( \Delta \delta / (J \text{ cm}^{-3})^{1/2} \) |
|----------|-------------|-----------------------------------|-----------------------------------|
| asphalt 1| 3.821×10⁸   | 19.54                             | 4.01                              |
| asphalt 2| 3.542×10⁸   | 18.82                             | 3.29                              |
| asphalt 3| 3.533×10⁸   | 18.79                             | 3.24                              |
| asphalt 4| 3.546×10⁸   | 18.83                             | 3.30                              |
| rubber   | 2.37×10⁸    | 15.53                             |                                   |
difficult it is to be compatible. When the molecular weight of the rubber powder is constant, the more the macromolecules contained in the asphalt, the greater the difference in energy between the asphalt and the rubber powder, and the poorer the compatibility between the two.

**Interaction Energy.** The nature of the compatibility of the two polymers is the interaction between the molecules, the size of which can be expressed by the interaction energy between the molecules:

\[
E_n = E_{abn} - E_{an} - E_{bn} \tag{4}
\]
\[
E_v = E_{abv} - E_{av} - E_{bv}
\]
\[
E_e = E_{abe} - E_{ae} - E_{be}
\]

\(E_n\), \(E_v\), and \(E_e\) represent the molecular interaction energy between the copolymers a and b, the van der Waals interaction energy, and the electrostatic interaction energy (kJ/mol); \(E_{abn}\), \(E_{abv}\), and \(E_{abe}\) respectively, represent the total molecular potential energy, van der Waals potential, and electrostatic potential energy (kJ/mol) of the mixture after copolymers a and b are mixed; \(E_{an}\), \(E_{av}\), and \(E_{ae}\) represent the total potential energy of the copolymer a, van der Waals potential, and electrostatic potential energy (kJ/mol); \(E_{bn}\), \(E_{bv}\), and \(E_{be}\) represent the total molecular potential energy, van der Waals potential, and electrostatic potential energy (kJ/mol) of copolymer b, respectively.

Molecular potential energy is the force due to the interaction between molecules, so the positive and negative potential energies are determined by the positional relationship. When the intermolecular distance is greater than the equilibrium distance, the molecular force is gravitation. When the distance increases, the molecular force performs negative work, and the molecular potential energy exhibits a negative value and vice versa.

The molecular potential energies of the four asphalt, rubber powder, and four blend models are shown in Tables 5-7. It can be seen from Table 5 that the total potential energy of asphalts 1 and 4 is higher than the total potential energy of asphalts 2 and 3, which indicates that the internal interaction of the 1 and 4 asphalt molecules is strong and the structure is relatively stable. It will weaken its interaction with the rubber powder, resulting in poor compatibility.

According to the data in the table and formula 4, the molecular interaction energy, van der Waals interaction energy, and electrostatic interaction energy between the four kinds of asphalt and rubber powder can be calculated. The calculation results are shown in Table 8.

**Table 8. Molecular Interaction Energy between Different Asphalts and Rubber Powder**

| Sample | 1& rubber | 2& rubber | 3& rubber | 4& rubber |
|--------|-----------|-----------|-----------|-----------|
| \(E_n\) | -2735.236 | -3277.681 | -3369.994 | -2454.904 |
| \(E_v\) | 641.205   | 691.910   | 702.678   | 669.143   |
| \(E_e\) | 667.420   | 625.175   | 669.066   | 693.425   |

It can be seen from Table 8 that the interaction between the no. 3 asphalt and the rubber powder is the largest; the no. 2 asphalt is the second, and the no. 1 asphalt is the smallest. It shows that the interaction between the no. 3 asphalt and the rubber powder is the strongest. This is because the light components contained in the no. 3 asphalt are more, and the rubber powder absorbs the light components during the swelling process to form a network structure. Make the blend system more stable. The light components in asphalt can fill the gap between the large components of the asphalt and the molecules of the rubber powder so that the distance between the two molecules becomes smaller. Because the van der Waals potential energy and electrostatic potential energy between the four kinds of asphalt and rubber powder are repulsive, the smaller the distance between molecules, the larger the van der Waals potential energy and electrostatic potential energy, the stronger the interaction, the more stable the blending system, and the more compatible the system. It can be seen that the order of compatibility of asphalt and rubber powder is: no. 3 > no. 2 > no. 4 > no. 1.

**Radial Distribution Function.** The radial distribution function \(g_{inter}(r)\) is a characteristic physical quantity that reflects the microstructure of the material, and it represents the ratio of the probability density of another molecule at a distance of \(R\) around one molecule to the probability density of random distribution where the distance around a molecule is \(r\). The hydrogen bonding force range \(r\) is 2.6–3.1 Å, and the van der Waals force range \(r\) is 3.1–5.0 Å. In addition, Lin et al. believe that if the radial distribution function between molecules of the same component in the blend is lower than that of the blend component, the probability of different molecules around a molecule in the blend is greater than that of the same molecule, indicating that two different molecules are compatible. The higher the radial distribution function \(g(R)\) of the blends is, the better the compatibility is.

It can be seen from Figure 6 that the radial distribution function between the rubber powder and each asphalt molecule does not show a peak at 2.6–3.1 Å, indicating that the main mode of action between the molecules is van der Waals force. The \(g_{inter}(r)\) of the blends of the four-rubber powder-modified asphalts was higher than the \(g_{inter}(r)\) of single-component asphalt or rubber powder, indicating that the four asphalts are compatible with the rubber powder. Among them, the difference between the \(g_{inter}(r)\) of the rubber powder-modified asphalt and the \(g_{inter}(r)\) of the single component is the largest, indicating that the compatibility is the best; the blend of the rubber powder-modified asphalt no. 2 and no. 4. The difference between the \(g_{inter}(r)\) and \(g_{inter}(r)\) of the single component is not much different, but the \(g_{inter}(r)\) of the blend in the rubber powder-modified asphalt is better.
of no. 2 is more different from the $g_{inter}(r)$ of the rubber powder. The compatibility is better than no. 4; the difference between $g_{inter}(r)$ and the single-component $g_{inter}(r)$ of the blend of no. 1 rubber powder-modified asphalt is the smallest, and the compatibility is the worst. The compatibility is in good agreement with the analysis of solubility parameters and molecular potential energy.

**Experimental Verification.** The base asphalt was heated to 160 °C, sheared at a high-speed shear at 3000 rpm for 20 min, and then 20% (mass fraction) of 60 mesh crumb rubber was added to heat and stabilize the asphalt temperature to 180 °C. Adjust the speed of the high-speed shear to 5000 rpm and shear for 1 h. Finally, it was placed in an oven at 160 °C for 1 h to prepare four kinds of crumb rubber-modified asphalt. The four-crumb rubber-modified asphalts were tested for the separation softening point of different asphalt binders according to JTG E20-2011 “Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering”. The results are shown in Table 9.

![Figure 6. Intermolecular radial distribution function of rubber powder and four asphalt blends: (a) no. 1 asphalt and rubber powder; (b) no. 2 asphalt and rubber powder; (c) no. 3 asphalt and rubber powder; and (d) no. 4 asphalt and rubber powder.](https://doi.org/10.1021/acsomega.2c02813)

| number | sample         | softening point difference/°C |
|--------|----------------|-----------------------------|
| 1      | asphalt 1 & rubber | 3.7                         |
| 2      | asphalt 2 & rubber | 3.3                         |
| 3      | asphalt 3 & rubber | 2.1                         |
| 4      | asphalt 4 & rubber | 2.9                         |

It can be seen from Table 9 that the softening point differences of the four modified asphalts are different under the conditions of the same preparation process. Among them, the difference of the separation softening point of no. 3 rubber powder-modified asphalt is the smallest. From the macroscopic point of view, the compatibility of no. 3 asphalt with crumb rubber is the best, and the previous simulation results have also been verified.

**Gray Relational Analysis.** Through the above MD simulation analysis, it can be seen that the compatibility of the crumb rubber with the asphalt of four different origins is...
different, mainly caused by the difference in the four components of the asphalt. Further analysis is needed to determine which component of the four components of the asphalt has the greatest impact on its compatibility.

The gray relational analysis method can systematically analyze the correlation degree between the asphalt components and the crumb rubber compatibility. This method has no strict requirements on the size and distribution of the data, and the calculation amount is relatively small, so it is widely used. First, select the reference sequence, denoted as \( x_0 = (x_{01}, x_{02}, \ldots, x_{0n}) \) and determine the comparison sequence, denoted as \( x_i = (x_{i1}, x_{i2}, \ldots, x_{in}) \). Under the determined \( k \) condition, the correlation coefficient of the reference sequence \( x_0 \) and the comparison sequence \( x_i \) can be expressed by \( \epsilon_i \).

\[
\epsilon_i = \frac{m + \rho M}{\Delta_i + \rho M}
\]

(5)

where \( \Delta_i = \max_j \{x_{ji} - x_{0j}\} \), \( \Delta_{ij} \) represents the difference sequence between the reference sequence and the comparison sequence; \( M = \max \Delta_i \), \( m = \min \Delta_i \), where \( M \) and \( m \), respectively, represent the maximum and minimum values in different sequences; \( \rho \) is the resolution coefficient and generally takes a value of 0.5.

Then, the degree of association between \( x_0 \) and \( x_i \) is

\[
\gamma_i = \frac{1}{n} \sum_{k=1}^{n} \epsilon_i(k)
\]

(6)

The solubility parameter and molecular potential energy data in the above MD simulation were selected as the reference series \( x_{0p} \) and the four components of the asphalt were used as the comparison series \( x_i \). The correlation between the four components of asphalt and the solubility parameters and molecular potential energy was analyzed by the gray correlation method. The four components of asphalt are shown in Table 1. The solubility parameter data is shown in Table 4. The molecular potential energy data is shown in Table 8.

The correlation between the four components of asphalt and the solubility parameters and molecular potential energy was calculated using MATLAB software. The results are shown in Table 10.

Table 10. Gray Correlation

| sample | As  | S   | Ar  | R   |
|--------|-----|-----|-----|-----|
| \( \Delta \) | 0.5516 | 0.9112 | 0.8556 | 0.8032 |
| \( E_s \) | 0.5711 | 0.8974 | 0.8772 | 0.7797 |
| \( E_0 \) | 0.5565 | 0.9157 | 0.8721 | 0.7725 |
| \( E_r \) | 0.5485 | 0.9124 | 0.8481 | 0.7908 |

It can be seen from Table 10 that the gray correlation degree between the four components of the asphalt and the solubility parameter is sorted by size: \( S > Ar > R > As \), and the order of correlation between the four components of the asphalt and the molecular potential energy is the same as above. It can be seen that the impact of asphalt lightweight components on asphalt compatibility is greater than that of asphalt heavy components. This is because light components can be absorbed by rubber powder and cross-linked to form a network structure, which makes the structure more stable and offers better compatibility.

## CONCLUSIONS

In this paper, four groups of micromolecular models of asphalt and rubber were established. The MD simulation method was used to study the influence of different asphalt component contents on the compatibility between rubber powder and asphalt. The main conclusions are as follows:

1. The cohesive energy density and solubility parameters of different asphalt and rubber powder show that the solubility parameter difference between Esso asphalt and rubber powder is the smallest. This is because the asphaltene and gum content in Esso is low and the number of macromolecules contained in Esso is small, which makes the energy difference between Esso and rubber powder smaller.

2. The molecular interaction between different asphalts and rubber powder shows that the Esso asphalt has the best compatibility with rubber powder and the Karamay asphalt has the worst compatibility with rubber powder. Rubber powder will absorb light components in the swelling process, forming a network structure so that the blend system is more stable. At the same time, the light component of asphalt can fill the gap between the large component of asphalt and the rubber powder molecules so that the distance between the two molecules becomes smaller.

3. The radial distribution function between the rubber powder and each asphalt molecule appears at a peak value at \( 3.1−5.0 \) Å, indicating that the main interaction mode between molecules is van der Waals force. The difference between \( g(R) \) of the rubber powder-modified asphalt blend with more light components and \( g(R) \) of single rubber is larger and has better compatibility.

4. The gray correlation degree of the four components of asphalt with solubility parameters and molecular potential energy is in the order of \( S > Ar > R > As \); that is, the impact of the light components of asphalt on the compatibility of modifying asphalt is greater than that of the heavy components of asphalt.

The results provide a theoretical basis for the research and development of high-performance rubber-modified asphalt. In future industrial production, the rubber powder-modified asphalt prepared with more light components will have better performance and storage stability.

## AUTHOR INFORMATION

### Corresponding Author

**Mingxing Gao** — College of Energy and Transportation Engineering, Inner Mongolia Agricultural University, Hohhot, Inner Mongolia 010018, China; orcid.org/0000-0002-6133-1327; Email: gaomingxing_2000@imau.edu.cn

### Authors

**Yaolu Chen** — College of Energy and Transportation Engineering, Inner Mongolia Agricultural University, Hohhot, Inner Mongolia 010018, China

**Conghao Fan** — College of Energy and Transportation Engineering, Inner Mongolia Agricultural University, Hohhot, Inner Mongolia 010018, China

**Meijian Li** — College of Energy and Transportation Engineering, Inner Mongolia Agricultural University, Hohhot, Inner Mongolia 010018, China

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c02813

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