The Influence of Styrene/butadiene Ratio on the Self-assembly Behavior of SBS Modified Asphalt

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Abstract. This work using molecular dynamic simulation to explore the micro mechanism of Styrene-butadiene-styrene (SBS) with light components (aromatics and saturates). The results indicate that the adsorption area decrease with the increase of S/B ratio. And with the increase of temperature, the adsorption area first increased and then decreased. Rutting factor experiments show that the rutting factor gradually decreases with increasing temperature and decreases with increasing S/B ratio, which is consistent with the findings of molecular dynamics simulations.

Keywords: Molecular dynamic simulation, Temperature stability, SBS modified asphalt;

1. Introduction

Styrene-butadiene-styrene (SBS) modified asphalt has become the most widely used type of modified asphalt due to its high-temperature and low temperature properties [1]. However, the styrene/butadiene (S/B) ratio and temperature have a significant effect on the interaction of SBS with the light components [2]. Styrene-butadiene-styrene (SBS) modified asphalt has become the most widely used type of modified asphalt due to its high-temperature and low temperature properties [1, 2]. Although SBS-modified asphalt technology has been used for many years, it still faces the challenge of poor storage stability due to phase separation, which greatly limits the application of SBS-modified asphalt [3, 4]. Generally, SBS-modified asphalt is a mixture of base asphalt and SBS polymer [5]. Under the condition of high temperature and high shear, SBS dispersed in the base asphalt. Due to absorption of light components (aromatics and saturates) from the base asphalt, the SBS polymer expanded, and increasing its volume by 4-10 [6, 7]. Moreover, the polystyrene (PS) segments of different SBS polymers connect with each other and form a three-dimensional phagocytic network containing the entire asphalt system, thus greatly improving the performance of the asphalt. At the microscopic scope, SBS-modified asphalt is a two-phase system composed of polymer-rich phase and asphaltene-rich phase. The morphology and properties of the two phases are affected by the polymer content [8-10]. However, due to the differences in density, molecular weight, polarity, solubility parameters and other properties, the polymer-rich and asphaltene-rich phases are prone to separation. At present, it is widely believed that the phase separation of modified asphalt is the main factor affecting the performance of polymer modified asphalt, because it will seriously damage the microstructure of polymer modified asphalt and make the modification ineffective [10, 11]. The objective of this paper is to explore the influence of S/B ratio and temperature on the phase separation of SBS-modified asphalt by molecular dynamics simulation. The molecular dynamics simulation of SBS-modified asphalt with three S/B ratios were carried out. The adsorption was characterized by the relative concentration distribution of mountain area. At the same time, the simulation results are verified by rutting factor experiment.
2. Methods

2.1. Molecular Models of Asphalt
As shown in figure 1 Asphaltene A, asphaltene B, and asphaltene C are used to represent asphaltenes. Aromatic A and aromatic B are used to represent aromatics. Saturate A and saturate B are used to represent saturates. Resin A, resin B, resin C, resin D and resin E are used to represent resins. In this paper, three kinds of SBS molecular chains with different S/B ratios (5/25, 7/18 and 9/10) were constructed in total, and three kinds of SBS modified asphalt models were further constructed, the content of SBS polymer in SBS-modified asphalt constructed in this study is 5%.

2.2. Molecular Models of SBS Modified Asphalt
The molecular models of virgin asphalt, 5/25 SBS modified asphalt, 7/18 SBS modified asphalt and 9/10 SBS modified asphalt constructed in this paper are shown in figure 2. The Geometry Optimization and Anneal operations have been performed on each SBS-modified asphalt. Therefore, molecular dynamics simulation was conducted directly on each model, and the pressure was set at 0.000101 Gpa. The dynamics simulation under the NVT ensemble of 100 ps was carried out first, and then the dynamics simulation under the ensemble of 100 ps NPT was carried out. The first 100 ps was for the energy and high force in the dispersion model, and the last 100 ps is to dissipate the mechanical forces in the model. It is worth noting that the simulated temperatures were respectively set at 298 K (25 °C, normal temperature), 338 K (65 °C, near the softening point) and 438K (165 °C, construction state temperature), which means that each SBS-modified asphalt must be simulated at 200 ps.
molecular dynamics at these three temperatures. Finally, the obtained stable structure, that is, the last frame of the dynamic simulation is analyzed microscopically. In addition, COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field was used throughout the study; it is a kind of ab initio force field widely used in condensed matter physics and polymer performance prediction [12].

Figure 2. Molecular model of common asphalt (a), 5/25 SBS modified asphalt (b), 7/18 SBS modified asphalt (c) and 9/10 SBS modified asphalt (d).

2.3. Rutting Actor Experiment
The base asphalt used in this research is SK90#. And three SBS polymers are used, their S/B ratios are 20/80, 30/70, and 40/60. In this paper, SBS-modified asphalt was prepared by melt blending method. First heat the asphalt into a fluid, and then add 5% SBS polymer into it, shear it in a high-temperature shearing machine at 3500 rpm for 30 min at a temperature of 175 °C, and then put the sample in the mixer stir at 1500 rpm for 3 hours at a temperature of 165 °C. The dynamic shear rheometer (DSR) used in the rutting test is SmartPave102 produced by Anton Paar GmbH in Austria. The rutting test standard is AASHTO T 315 (SHRP-test), and the fluorescence microscope for observing the micro morphology of SBS modified asphalt is the BML-400E.

3. Results and Discussion

3.1. Effect of S/B Ratio and Temperature on the Adsorption of SBS and Light Components
Figure 3. Relative concentration distribution of SBS polymer and light components.

The relative concentration distribution of SBS with different S/B ratios and the light components is shown in figure 3. The black line represents the relative concentration distribution of SBS polymer, and the red represents light components. It can be seen from figure 3 that there are obvious peaks of concentration in SBS, indicating that there is aggregation of SBS polymer. On both sides of the peaks of SBS polymer concentration, the concentration of light components often follows the peaks of SBS polymer concentration, indicating that the SBS polymer has obvious adsorption phenomenon to light components, which is consistent with the consensus of SBS-modified asphalt [2].

Figure 4. Adsorption areas of different S/B ratios and temperature.

The total area of SBS polymer adsorbed light components at different S/B ratios and temperatures are shown in figure 4. It can be seen that, for the SBS with S/B ratio of 5/15, when the temperature increased from 25 °C to 65 °C, the total area of SBS polymer adsorbed light components increased from 105.42 Å² to 112.53 Å². And when the temperature increased from 65 °C to 165 °C, the total area of SBS adsorbed light components decreased from 112.53 Å² to 85.56 Å². The total area of adsorbed light components of SBS polymers with S/B ratios of 7/18 and 9/10 also increased first and then decreased. For the same temperature, with the increase of S/B ratio, the total asphalt adsorbed by SBS always decreases gradually. For example, at 25 °C, when the S/B ratio increases from 5/25 to 9/10, the total adsorption area also decreases from 105.42 Å² to 99.09 Å², and from 96.70 Å². Combining the data of diffusion coefficient and binding energy, it can be seen that the law of adsorption area is consistent with that of binding energy and diffusion coefficient, which indicates that S/B ratio and
temperature have great influence on the two-phase behavior of SBS polymer and asphalt. In other words, when the S/B ratio gradually increases, SBS polymers are more prone to phase separation. At the same time, in the SBS-modified asphalt system with a larger S/B ratio, the polymer-rich phase should be smaller. Compared with SBS polymers with a small S/B ratio, SBS polymers with a large S/B ratio not only have small interaction with asphalt and slow diffusion, but also absorb fewer light components of asphalt.

3.2. Rutting factor of Three SBS Modified Asphalts
The rutting factor data further validated the simulation results. We measured the rutting factors of three SBS-modified asphalts at 35 °C, 45 °C, 55 °C and 65 °C. The results are shown in figure 5. Regardless of the temperature, with the increase of S/B ratio, the rutting factor of modified asphalt decreases, which is consistent with the conclusion of molecular dynamics simulation. For the same SBS-modified asphalt, as the temperature increases, the rutting factor also decreases. This is because the test temperature is low, followed by the presence of a large amount of asphaltenes and gums in the modified asphalt system, which have a significant impact on the properties of the modified asphalt.

Figure 5. Rutting factors of three modified asphalts at different temperatures.

4. Conclusions
Molecular dynamics simulations were used to explore the ability of temperature and S/B block ratio on SBS adsorption of lightweight components, and rutting factor experiments were used to validate the results of molecular dynamics simulations.

With the increase of temperature, the adsorption area of SBS and light components always increase first and then decrease. This is because the higher the temperature, the greater the energy in the system, the greater the kinetic energy obtained by SBS polymer, the faster its diffusion and flow, the higher the diffusion coefficient. The reason why the binding energy and adsorption area decrease is that the temperature is already higher than the glass transition temperature of PS segment, the PS segment cross-linked with each other has been separated, and the three-dimensional polymer network in the SBS modified asphalt system has been destroyed. Therefore, the binding energy and adsorption area of SBS polymer and the light components have been reduced. The rutting factor image shows that as the S/B ratio increases, the rutting factor of the modified asphalt decreases. These all echo the results of molecular dynamics simulations.

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