Enhancement of Compatibility of SBS Modified Asphalt by CNTs: Interpretation from Dissipative Particle Dynamics Simulations

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Abstract. The compatibility of styrene-butadiene-styrene (SBS) with base asphalt is known to restrict the application of SBS modified asphalt. In this study, carbon nanotubes (CNT) were used to enhance the compatibility between SBS and base asphalt. The effect of CNTs on the compatibility of SBS modified asphalt was investigated by dynamic mechanics analysis (DMA), and the micro-mechanism of CNTs enhancing the compatibility of SBS modified asphalt was studied by using dissipative particle dynamics (DPD) simulation. The results show that CNTs can significantly improve the compatibility between SBS and base asphalt, and the microscopic mechanism is that CNTs can change the distribution morphology of SBS in base asphalt, making the distribution of SBS modified asphalt more uniform, which promotes the development of polymer-rich phase in SBS modified asphalt. This study can provide theoretical guidance for the practical application of SBS modified asphalt.

Keywords: SBS modified asphalt, Dissipative particle dynamics simulation, CNTs; Compatibility mechanism

1. Introduction
Styrene-butadiene-styrene (SBS)-modified asphalt is currently the main material for road construction, and its usage is probably the largest of all materials in the world [1]. However, SBS-modified asphalt faces the challenge of insufficient compatibility between SBS and base asphalt at high temperatures, which leads to the tendency of phase separation when stored at high temperatures and seriously weakens the road performance of SBS modified asphalt [2]. Many researchers have explored the compatibility problem of SBS modified asphalt and concluded that adding a small amount of solubilizer to SBS modified asphalt can effectively alleviate the phase separation problem, among which carbon nanotubes (CNTs) have received much attention because of their unique structure [3].

Although there have been some studies on the use of CNTs to enhance SBS modified asphalt, unfortunately the enhancement mechanism of CNTs on the compatibility of SBS modified asphalt is still not well understood [4]. The reason is that most of the previous experiments used are macroscopic scale to explore the effect of CNTs on the road performance of SBS modified asphalt, while the mechanism at the microscopic scale is often described by fluorescence microscopy and other methods for qualitative appearances, which cannot lead to in-depth universal conclusions [5]. And a number of researchers have started to focus on the use of molecular dynamics simulation in recent years, but it is still difficult to explore the dynamic behavior of such aggregates of SBS modified asphalt at the
molecular scale. However, dissipative particle dynamics (DPD) simulations can overcome this drawback well [6].

In this study, CNTs were used to capacitate SBS modified asphalt, and a coarse-grained model of CNTs/SBS modified asphalt was constructed and DPD simulations were performed to deeply analyze the fine-scale mechanism of CNTs on the compatibility enhancement of SBS modified asphalt. Finally, the simulation results were verified using dynamic mechanical analysis. This study can provide theoretical support for the improvement of the compatibility of SBS modified asphalt.

2. Methodology

The first step to a successful DPD simulation is the construction of a reasonable coarse-grained model, which is built on the basis of a molecular model. Asphalt is an extremely complex mixture, which contains millions of molecular species, and it is impossible to construct a true molecular model of asphalt. Currently, asphalt is often divided into three or four components. In this study, a four-component model is used, and one molecule is used instead of one component. The average four-component molecular models of asphalt used in this study are shown in figure 1, and based on this, this study coarsely grains these molecular models.

![Figure 1](image_url)

**Figure 1.** Average molecular model for asphaltene (a), gum (b), aromatic fraction (c) and saturated fraction (d).

According to the DPD simulation calculation requirements and Flory-Huggins theory, each bead after coarse granulation must maintain the same volume. In the DPD simulation of this study, the volumes of various molecules are calculated first, then the maximum common multiple of these volumes is found, and then the calculated maximum common multiple is used as the volume of the DPD simulated beads. Based on this, the number of molecules represented by each bead can be
obtained.

As shown in figure 2, one bead A represents 4 saturated fractions, one bead B represents 2 aromatic fractions, one bead C represents 2 gums, and one bead D represents 1 asphaltene; in addition, one bead E replaces 12 styrene monomers and one bead F represents 17 butadiene monomers. For better observation of the simulation results, the authors used a box size of 200 × 200 × 200 (DPD simulation size) and the density was set to 3 g/cm³. i.e., the relationship between the bead-to-bead repulsion parameters and the Flory-Huggins parameters is shown in equation (1).

\[ a_{ij} = a_{ii} + 3.27 \chi_{ij} \]  

(1)

where \( \chi_{ij} \) is the Flory-Huggins parameter between both bead \( i \) and bead \( j \), and \( a_{ii} \) is 25.
Figure 2. DPD simulation bead model for SBS polymer (a), asphaltene (b), gum (c), aromatic fraction (d) and saturated fraction (e).

Suppose the ratio of asphaltene, gum, aromatic fraction, saturated fraction and SBS in SBS modified asphalt composite is 1:3:7:5:1. The temperature of the simulation process is set to 1, and its corresponding experimental temperature is 298 K. The simulation step is 200000, and the time step is set to 0.005, so the total simulation duration is 1000ps, and one frame is output every 1000 steps, and the last frame is taken frame for analysis. It is proved that the time is sufficient for the system to reach kinetic equilibrium, and the energy change of the whole simulation is shown in figure 3. The energy of the two systems in figure 3 finally tends to be smooth, which means that the system is in kinetic equilibrium.

Figure 3. Energy change during DPD simulation.
3. Results and Discussion

3.1. Flory-Huggins Interaction Parameters

|                | Asphalt | SBS    | Carbon  |
|----------------|---------|--------|---------|
| Asphalt        | 0       | 246.7  | 240.7   |
| SBS            | 246.7   | 0      | 166.1   |
| Carbon         | 240.7   | 166.1  | 0       |

The Flory-Huggins parameter was calculated using the Blends module of Materials studio to determine the compatibility between the two molecules and to provide a basis for DPD simulations, and the results are shown in table 1. The larger the value of the Flory-Huggins parameter, the stronger the degree of incompatibility of the components, indicating possible phase separation. Higher values of Flory-Huggins parameters indicate a stronger degree of incompatibility of the components, predicting a possible phase separation. Higher values of the parameters between SBS and asphalt (246.7) indicate a poor compatibility between SBS and asphalt. The parameter values decrease in the presence of carbon nanotubes (166.1-240.7). Therefore, the carbon nanotube/SBS/asphalt system is more compatible than the SBS/asphalt system, which means that the carbon nanotubes improve the compatibility of SBS polymer with asphalt.

3.2. Microscopic Appearance

In general, the processing properties and comprehensive performance of polymer-based systems depend largely on the system microstructure and distribution state [1, 2]. The effect of 0.3 Wt.% carbon nanotubes on the microscopic morphology of SBS polymer in the system was investigated by DPD (DPD) simulations, in which the microscopic morphology of SBS polymer is shown in figure 4. Apparently, an ordered structure of SBS polymer was formed in the SBS/asphalt system (for the convenience of observation, the asphalt four components and carbon nanotubes were removed, leaving only SBS polymer). The microscopic morphology of the SBS polymer in the carbon nanotube/SBS modified bitumen and SBS modified bitumen systems is clearly different; for the SBS modified bitumen, the SBS polymer in the system is lattice-like, while the SBS polymer in the carbon nanotube/SBS modified bitumen is clearly layered. Since there is only one variable of carbon nanotubes in both systems, it can only be carbon nanotubes that change the microscopic morphology of SBS polymer in the system from lattice-like to lamellar.

![Figure 4. SBS modified asphalt (a) Carbon nanotube/SBS modified asphalt (b) distribution of system SBS polymer after DPD simulation (green represents polystyrene segment and gray represents](image-url)
3.3. Road Performance of SBS/Asphalt Composites

The rutting factors of SBS modified asphalt and CNTs/SBS modified asphalt are shown in figure 5. CNTs can increase the rutting factor of SBS/asphalt generally between 64 and 88°C. In addition, CNTs can increase the softening point of SBS modified asphalt from 70.1°C to 72.4°C. As mentioned earlier, the improvement of road performance is closely related to the compatibility of SBS/asphalt, and it was found that the rutting factor and softening point of SBS modified asphalt were generally increased after the addition of carbon nanotubes, which indicates that the addition of carbon nanotubes enhanced the compatibility of SBS modified asphalt.

![Figure 5. Rutting factor at different temperatures.](image)

4. Conclusions

The microscopic mechanism of CNTs on the compatibility enhancement of SBS modified asphalt was explored using DPD simulations, and it was found that CNTs can enhance the compatibility of SBS polymer with base asphalt, because CNTs can significantly improve the distribution of CNTs in the base asphalt again, making SBS more uniformly distributed, which will promote the absorption of light components in the base asphalt and enhance the performance of SBS modified asphalt is enhanced.

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