Molecular Dynamics Simulations on Polymer-Modified Model Asphalts

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Abstract

Adding polymers to asphalt binder has shown to increase the performance of asphalt. In this study, Molecular Dynamics simulation was performed to predict physical and transport properties of asphalt mixtures modified with several polymer modifiers. Polyethylene, polystyrene, and poly(styrene-butadiene) rubber were individually added to the ternary asphalt model mixture of Zhang et al. [1] and important properties were calculated. Each mixture was simulated at four different temperatures – ranging from 25 °C to 170 °C. Mass density, diffusion coefficients, and radial distribution functions were calculated for each simulation. It was found that different polymers can modify the model asphalt property and microstructure differently, and the simulation predictions can agree with experimental data.

Introduction

Asphalt is a very diverse mixture of organic molecules containing more than 1 million different molecules in a given sample. It is derived from crude oil, and is the remaining fraction after distillation. This viscous tar is called asphalt “binder” and is mixed with aggregate gravel to form road pavement, but asphalt pavement has problems with its performance in extreme conditions. For example, asphalt pavement is susceptible to cracking at low temperatures and rutting at high temperatures. This is primarily caused by a strong temperature susceptibility on its physical properties. For instance, the viscosity changes too greatly with a given change in temperature [2]. Additives such as polymers have helped mitigate low-temperature fatigue cracking in asphalt pavements. In order to know what kind of polymer modifier should be added, and how much polymer should be added, understanding the relationships between the chemical composition, microstructure and physical and mechanical properties of asphalt is important. Molecular dynamics simulation is the desired way to supply such kind of information.

In order to do simulations on complicated asphalt mixture, different analyses were done. SARA analysis is an analysis which classifies crude oil based on solubility in organic solvents. Molecule types are saturates, aromatics, resins, and asphaltenes. Classification of the different types of molecules found in asphalt mixtures allows for the construction of a model to be built to approximate the properties of asphalt using computer simulation programs. The ternary model of Zhang et al. was used in these simulations to approximate asphalt binder without aggregate [1]. It is comprised of 5 asphaltene2 molecules, here asphaltene2 is a averaged asphaltene molecule, 30 1,7-dimethylnaphthalene molecules, and 45 n-
C22 molecules with molecular structures and compositions of model asphalt mixture (as2) shown in Figure 1. This ratio best approximates the composition and properties of true asphalt mixtures [3].

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Molecular Dynamics (MD) programs utilize equations of classical mechanics to displace atoms in a simulation box. In many cases, small systems can be simulated to predict macroscale properties of substances. MD programs such as LAMMPS simulations, can lead to an understanding of the behavior of substances on a molecular scale. Periodic Boundary Conditions (PBC) play an important role in MD program, because they allow for a continuous medium in which intermolecular interactions can be calculated without worrying about the surface effect. Figure 2 shows that if a particle passes through the side of the simulation box, it will be accounted for by moving its imagine into the same box from the opposite side. PBC allow for macroscopic properties to be calculated by actually simulating only several thousand atoms.

Figure 1
The ternary model asphalt (as2) used in these simulations is comprised of
(a) 5 asphaltene2 [15] molecules
(b) 30 1,7-dimethylnaphthalene molecules
(c) 45 n-C22 molecules.
The addition of a polymer to asphalt binder has proven to change rheological properties of asphalt pavement [4], thus mitigate pavement cracking problems. Another benefit of polymer modification is the reduction of temperature susceptibility of the asphalt binder — the primary factor in improving cracking resistance. Problems still exist with compatibility between asphalt binder and certain polymers. Asphalt-soluble polymers should be chosen in order to ensure property consistency throughout the mixture. Aromatic oil is commonly added to improve the compatibility between polymers and asphalt [5].

Studies have shown adding polymers such as polystyrene-butadiene-styrene (SBS) and styrene-butadiene rubber (SBR) have experimentally improved performance of asphalt binder by modifying its physical and elastic properties. The primary method of determining the improvement of polymer-modified asphalt is the evaluation and comparison of: density, viscosity, thermal expansion coefficient, softening point, and modulus. Since polymer modification has been a topic of research for years, prior research has provided some guidance in choosing optimal polymers for asphalt modification. Popular polymers used in asphalt modification are styrene-butadiene styrene (SBS) triblock copolymer and styrene-butadiene rubber (SBR) [4]. Other polymers such as acrylate-styrene-acrylonitrile (ASA), polyethylene (PE), ethylene vinyl acetate (EVA), and natural rubber are potential modifiers [6] [7] [8]. Experimentally, it was determined PE does not mix well with asphalt binder. Storage stability analysis showed the PMA separated into two phases [9]. Polymers have been chosen based on cost-effectiveness, availability, and prior knowledge of improving asphalt mixtures. In this project, the polymers to be simulated with model asphalt are: polyethylene, polystyrene, and styrene-butadiene rubber.

Prediction of major physical and mechanical properties of model asphalt in a controlled environment, such as a computer program, allows researchers to compare properties of unmodified asphalt to polymer-modified asphalt with a control of molecular ratios and length of polymer chains. In this research, in total three polymers as listed above were studied for their effects on the microstructure and macroscopic properties of model asphalt binders through the use of Molecular Dynamics simulations.

Simulation Methods

Realistic polymers have high molecular weights and typically have thousands of monomers in one molecule. In this study, polymers were shortened to minimize computation time without compromising accuracy of the simulations. The length of each polymer molecule was limited to 50 monomers. Table 1 contains details about each simulation. The mixtures were simulated at 298.15 K, 358.15 K, 400.15 K, and 443.15 K. The upper bound of this temperature range corresponds to the mixing temperature of hot-mix asphalt [10].
A combination of Molecular Dynamics (MD) and Monte Carlo (MC) programs was used to simulate these systems to reach an equilibrated state. After the equilibrated state was reached, physical properties were calculated. The Monte Carlo for Complex Chemical Systems (MCCCS) Towhee program [11] was used to initialize the structures of each molecule type before simulating the mixtures. The MD program Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [12] was used to equilibrate the systems.

The All-Atom Optimized Potential for Liquid Simulations (OPLS-aa) force field was used. After an optimal structure was obtained for each molecule type, the mixture system was initialized by placing different types of molecules on a cubic lattice in Towhee. The isobaric-isothermal (NPT) ensemble was used in LAMMPS to equilibrate the systems. After equilibrium was achieved, physical and microstructural properties were calculated. Density, diffusion coefficients, and radial distribution functions were calculated for the mixtures.

Density was output from LAMMPS automatically. Diffusion Coefficients were calculated for each molecule type using the mean-square displacement (MSD) of each molecule, also known as the Einstein Relation [13]. Equation 1 relates the diffusion coefficient, D, to time, t, and position, r. Diffusion Coefficients were calculated by averaging the MSD for each molecule type at each step. These displacements were plotted over a time interval of at least 8 ns and fit to a linear regression line. The slope of that line is proportional to D.

\[
2tD = \frac{1}{3} \langle |r(t) - r(0)|^2 \rangle
\]

Equation 1

The pairwise radial distribution function, g(r), is a probability density function used in determining packing distances between atoms or molecules. Here, g(r) was calculated between same and different molecule types. To closely approximate the center of mass g(r) for molecule types, one atom near the center of mass was chosen to represent the molecule. The radial distribution functions were calculated over a trajectory of more than 4 ns to maximize statistical accuracy.

Results and Discussion

The calculations presented here were all calculated from an equilibrated simulation. Each simulation was performed for at least 10 ns before calculating these properties.

Density

Mass density was calculated for each system at the four temperatures. Figure 3 shows the relationship graphically. The relationship between density and temperature was shown to be linear. Polyethylene did not significantly change the density of the model asphalt, while polystyrene and SBR increased the density.
This is likely due to two factors. The mass fraction of PE is small (5.8 %), and the density (at 25 °C) of low density polyethylene (LDPE) is 0.91 – 0.96 g/ml [REF]. A mixture of LDPE and the model asphalt in this proportion should not be expected to have an increased density. PS and SBR both increased the density of the ternary model asphalt. This behavior is likely attributed to the large mass fractions of PS and SBR (18.64 %, and 14.74 % respectively). A large mass fraction and a large difference in densities of asphalt binder and these polymers are likely to explain this behavior of increased densities.

**Diffusion Coefficient**

The diffusion coefficient is a measure how fast a particle moves through a medium. It can be calculated with MD by measuring the average displacement of a particle over time.

The diffusion coefficient for each component was calculated. On a logarithmic scale, the diffusion coefficients of each constituent increased with respect to temperature fairly linearly. Poor statistics contributed to the nonlinear relationships observed in Figure 4.

Molecular weight was shown to have an effect on the diffusion coefficient. The heaviest molecules diffused slowest. PE diffused the fastest of the three polymers in asphalt. Generally, the addition of a polymer molecule increased diffusion coefficients of each asphalt constituent, which is consistent with prior calculations [2]. Poor statistics are most prevalent in the polymer and asphaltene results due to the averaging of 5 or fewer molecules.

**Radial Distribution Functions**

The pairwise radial distribution functions, \( g(r) \), is a probability density function used to determine the most probable distance between atom pair or molecule pair. In this work, it was calculated for asphaltene – asphaltene pairs, asphaltene – dimethylnaphthalene pairs, and dimethylnaphthalene – dimethylnaphthalene pairs. The first peak position, \( d_0 \), is the most probable distance in which atoms or molecules prefer to stay in relation to one another. The movement of \( d_0 \) indicates a change in microstructural packing. A first peak distance which has decreases after certain conditions have been applied to the system indicate a closer packing distance, since the most probable distance between the specified atoms decreased.
Asphaltene – dimethylnaphthalene and dimethylnaphthalene – dimethylnaphthalene pairs were not significantly affected by the addition of a polymer. Figure 6 and Figure 5 show the asphaltene – dimethylnaphthalene and dimethylnaphthalene – dimethylnaphthalene pairs respectively for the simulations at 443 K. At 298 K, 358 K, and 400 K, similar behavior was observed. The g(r) did not significantly change upon the addition of a polymer. Since the behavior and d0 of these distribution functions remained about the same, the addition of polymer modifiers is not likely to affect packing distances between asphaltene and resin, nor resin and resin.

Changes to g(r) can be seen in Figure 7, which shows the radial distribution function for asphaltene – asphaltene pairs. These functions changed greatly with temperature and polymer identity. At 298 K, d0 between asphaltene molecules decreased when PE was added and increased when PS and SBR were added. At 358 K, d0 decreased upon the addition of PS, remained about the same when PE was added, and increased when SBR was added. At 400 K, both PE and SBR decreased d0, while the addition of PS did not show a first peak position near the others. At 443 K, the temperature at which asphalt binder is mixed with aggregate, d0 decreased upon the addition of PS and SBR, and increased after adding PE. First peak distances are expressed in Table 2.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Ternary Asphaltene2 systems</th>
<th>Polyethylene-Modified</th>
<th>Polystyrene-Modified</th>
<th>SBR-Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>7.775</td>
<td>3.675</td>
<td>9.275</td>
<td>10.28</td>
</tr>
<tr>
<td>358.15</td>
<td>8.875</td>
<td>9.325</td>
<td>4.975</td>
<td>8.275</td>
</tr>
<tr>
<td>400.15</td>
<td>4.775</td>
<td>3.875</td>
<td>11.537</td>
<td>3.725</td>
</tr>
<tr>
<td>443.15</td>
<td>7.275</td>
<td>9.325</td>
<td>7.075</td>
<td>4.545</td>
</tr>
</tbody>
</table>

These g(r) results are likely to reflect poor statistical sampling, because of the small system size. The model asphalt mixture sample used here contained only 5 asphaltene2 molecules. Distances between these asphaltene molecules may have been obstructed or constrained by other constituents or the added polymer. The systems were simulated for more than 10 ns in order to ensure equilibration of the model asphalt, yet more time may be needed for polymers to relax [14].

![Figure 6](image-url)  
Figure 6: asphaltene – dimethylnaphthalene g(r) at 443 K. The functions are essentially the same.

![Figure 5](image-url)  
Figure 5: dimethylnaphthalene – dimethylnaphthalene g(r) at 443 K. The functions are essentially the same.

![Figure 7](image-url)  
Figure 7: g(r) for asphaltene – asphaltene pairs at four different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Asphaltene2 Molecule Pairs in Original and Modified Ternary Asphaltene2 Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>First Peak Distance d0 (in Å) for Asphaltene2 Molecule Pairs in Original and Modified Ternary Asphaltene2 Systems</td>
</tr>
</tbody>
</table>
Microstructure

Different from quantitative calculations, some information can also be gathered from qualitative observations of the simulations. Aside from the theoretical benefits of PMA, it is vital to know realistic behavior of the materials. Polymers may be able to improve the physical properties and temperature susceptibility of asphalt, but realistic problems arise when having to transport, store, and implement asphalt binder.

Figure 8 shows the three polymers used in this work in their asphalt binder environments. PE did not interact with the model asphalt binder in the way PS and SBR interacted with the asphalt binder. This behavior is consistent with the biphasic separation observed in storage stability analysis by Polacco et al. [9]. Equilibrium trajectories were analyzed for 6 ns and it was found the structure of the PE molecule remained fairly linear and was not surrounded by saturate, resin, nor asphaltene molecules. PS and SBR appeared well-solvated by the asphalt constituents. 1,7-dimethylnaphthalene, PS, and SBR have aromatic features, which likely attributes to the solvation of these two polymers.

Conclusions

In order to understand polymer modification of asphalt binder on a molecular scale, computer simulations were used to quantify properties of unmodified model asphalt binder and model asphalt binder modified with polyethylene, polystyrene, and poly(styrene-butadiene) rubber. Density, diffusion coefficients, and radial distribution functions were calculated. Aside from quantitative analysis, it was also observed polyethylene is likely to be insoluble in asphalt binder. This observation is consistent with experiential observations in industry.

Through the use of Molecular Dynamics software, it was determined polyethylene, polystyrene, and SBR rubber may be appropriate modifiers in asphalt modification. More Molecular Dynamics simulations and experimental field testing should be performed for accuracy.

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References


