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Intrinsic temperature sensitive self-healing character of asphalt binders based on molecular dynamics simulations

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ABSTRACT

The molecular dynamics (MD) simulation was used in this study to explain the microscopic process of asphalt self-healing and investigate the influence of temperature on the self-healing capability of asphalt binders. Asphalt average molecular structure models of four types of neat asphalt binders were constructed firstly and a three-dimensional (3D) micro-crack model was further introduced to simulate the asphalt healing process. Based on the simulation results, the density analysis, relative concentration analysis, and mean square displacement analysis (MSD) were performed to investigate the temperature sensitive self-healing character of asphalt binders. Differential scanning calorimeter (DSC) test was adopted to get the phase transition (PT) temperature range of asphalt binders. The DSR-based fatigue-healing-fatigue test at different temperatures was also carried out to observe the self-healing capability of asphalt binders from the macroscopic view. According to the numerical and experimental results, it can be found that the molecular diffusion rate and diffusion range were more distinct especially within the PT temperature range, which indicated that the self-healing capability of asphalt was strong in PT temperature. Moreover, the results showed that there existed an optimal temperature range for asphalt healing, considering too high temperature may lead to permanent deformation, the optimal healing temperature range determined in this paper was 40.3–48.7 °C.

1. Introduction

Asphalt materials have intrinsic self-healing capability, which is explained by the surface energy of the system and diffusion of asphalt molecules from the matrix to the crack surface [1–3]. It is clear that the chemical composition and molecular structure of asphalt binder determine its self-healing capability, but it is difficult to establish their relationship based on the traditional test methods because of the complexity of its composition and structure. Actually, the initiation, propagation and possible healing of cracks all originate from molecular scale. The theory of continuum mechanics and traditional test methods cannot be adapted to the study in the microscopic field [4–6]. Recently, molecular dynamics (MD) simulations are widely applied to simulate the asphalt behavior at the molecular scale and could become a powerful tool for the study on the self-healing capability of asphalt materials.

MD simulation is a computer simulation method of the molecular movement of numerous N-body particles based on the physical principles of atoms and molecules [7–9], and the trajectories of atoms and molecules rely on Newtonian mechanics and are defined by the applied force filed. MD simulations provide more chemical details and potentially accurate short-time dynamic behavior, but require much more significant computational resources [10]. Actually, MD investigations on the molecular level can increase the fundamental understanding of the macroscopic phenomena of asphalt binder. In recent years, some excellent works have been done to study the physicochemical properties of asphalt binders, oxidative aging of asphalt binder, and asphalt-aggregate interface using MD simulations [7–9,11–15]. Zhang and Greenfield employed MD to estimate the properties of hypothetical asphalt binders [7,8,11]. They created a representative volume of an asphalt binder using molecules that represent chemical compositions in asphalt binders: asphaltenes, saturates, naphthene, aromatics, and polar aromatics. Xu et al. built 12-component aged and virgin asphalt models based on Materials Studio (MS) software, and found that aging weakened the nanoscopic aggregate behavior and reduced the translational flow of asphalt molecules [12]. With the aggregate represented by the quartz, Wang et al. constructed the asphalt-water-aggregate three-phase system to simulate the diffusion of water in the interface by using the CVFF force field [13].

However, limited works have been done on using MD to understand

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the self-healing behavior of asphalt binders. Bhasin et al. firstly introduced MD to asphalt healing analysis since 2011 [14], and used a three-component asphalt model and constructed a fracture model with a crack of 5 Å(1 Å = 10^{-10} m), which proved that the crack healing could be promoted by supplying the energy at an elevated temperature of 873 K. Similarly, Sun et al. also constructed a three-component asphalt model, a SBS modified asphalt model and an asphalt fracture model with a crack of 10 Å and thought that the diffusion coefficient increased with the increase of temperature [15]. They proved that high temperature was beneficial to the healing rate of asphalt, which was in line with the actual situation. Recently, Xu et al. constructed a two-layer asphalt model with 10 Å crack and used MD simulations to calculate the molecular diffusion capacity and activation energy of aged and virgin asphalt at different temperatures [12]. Results showed that the aged asphalt had lower molecule diffusion rate and higher activation energy barrier for self-healing compared to base asphalt. Moreover, it was also found that asphalt diffusivity increased with an increase in the temperature, for both the virgin and aged asphalt. Shen et al. built MD models with different crack widths to investigate the micro-mechanical healing mechanism of asphalt binder and characterize the influence of crack width on healing using an open-source code software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [16]. For the same crack length, asphalt heals faster when the width of crack is smaller. Besides, healing was found to be triggered by the diffusion mechanism of asphalt molecules, and higher temperature would result in higher diffusivity of molecules and thus higher healing rate.

Obviously, the healing temperature is a critical external factor that influences the self-healing capability of asphalt binders from the above conclusions. In fact, the asphalt binder may start flowing into the crack quickly when it is heated to suitable temperature (usually ranging from 30 °C to 70 °C, depending on the type of bitumen and aging level) [17–21]. Thus, the asphalt binder can reach a sufficient healing once reaching a certain temperature. If the temperature is too low, the crack will not be fully healed [22]. However, when the heating temperature is too high, it may reduce the healing level due to drainage of the asphalt under gravity [20]. Moreover, asphalt binders also tend to suffer more serious aging at higher temperature. Hence, each type of asphalt binder should have an optimal healing temperature. Tang et al. thought that the softening point temperatures of asphalt binders at the Newtonian fluid state are the optimal temperatures to heal fatigue damage [20]. Alessandro et al. found that the induction heating at 55 °C can achieve the optimum healing for the dense graded asphalt concrete containing steel fiber [19]. Liu et al. found that the fractured porous asphalt beams with 4.5% Pen 70/100 bitumen has an optimal heating temperature of 85 °C through induction heating [23]. Theoretically, different asphalt binders have different optimal healing temperatures, depending on the rheological properties of the binders [20]. At the same time, it is known that asphalt is likely to emerge permanent deformation at too high temperature, while the crack is more likely to occur at medium and low temperature [24]. Therefore, it needs further study to determine the critical temperature range which is most beneficial for the self-healing.

In this study, four base asphalt binders were selected to investigate their temperature sensitive self-healing character based on MD simulations. Firstly, the average molecular structure models of the asphalt binders were constructed based on the measured structure parameters, which was different from the previous studies in which they generally used the molecular models referenced from others' literatures [12,14–16]. For example, the SHRP average molecular structure [25], SHRP 12-component asphalt model [26] and a three-component asphalt model from Zhang and Greenfield [8,11] are usually used as the basis for their MD analysis. Then, a three-dimensional (3D) micro-crack model was further established to investigate the parameter variations related to the self-healing capability at different temperatures, especially within phase transition (PT) temperature range of the asphalt binders. Lastly, combined with the macroscopic fatigue-healing-fatigue (FHF) test employed by dynamic shear rheometer (DSR), the temperature sensitive self-healing character of asphalt binders was analyzed to determine the optimal temperature range for self-healing.

Table 1
Basic physical properties of base asphalt.

Binders' codes	Penetration (25 °C, 100 g, 5 s), 0.1 mm	Softening point (R & B), °C	Ductility (15 °C, 5 cm/min), cm
PEN 20	21.7	64.9	–
PEN 50	43.2	52.5	> 100
PEN 70	68.4	46.2	> 100
PEN 100	108.8	43.0	> 150

2. Materials and model developments

2.1. Thermal properties of asphalt binder samples

In this study, four penetration grades of base asphalt binders (PEN 20, PEN 50, PEN 70 and PEN 100, respectively) were selected to construct the corresponding average molecular models. They were all sampled from China Sinopec Company. The basic physical properties of four binders were shown in Table 1.

Asphalt is a typical temperature sensitive material and its physico-chemical properties vary greatly due to different temperatures. To obtain the thermal properties of four binders, the Differential scanning calorimeter (DSC) test was employed to measure the heat amount required to increase the temperature of a sample. The test conditions are listed in the following: 1) temperature range: −50 °C–100 °C; 2) heating rate: 10 °C/min; 3) sample weight: 2–5 mg; 4) test instrument: DSC Q2000; 5) reference material: indium (a kind of metal with high-purity). The test results are shown in Fig. 1. Thereby, the PT temperature range was determined by calibrating the marked endothermic peak, as listed in Table 2.

As shown in Fig. 1 and Table 2, the PT temperature range of the four binders was between 40.3 and 49.4 °C. When the temperature was lower than the PT temperature, there was no obvious peak on the DSC curve of PEN 20 and PEN 50, which proved that the asphalts absorbed less heat below the PT temperature. With respect to the PEN 70 and PEN 100, their phase transition occurred between 40.3 and 47.0 °C during the high temperature range. Moreover, it can be seen that there was obvious peak during the low temperature range on the DSC curve of PEN 70 and PEN 100 asphalt, which indicated PEN 70 and PEN 100 asphalt absorbed more energy than PEN 20 and PEN 50 asphalt in unit time at the low temperature (0–20 °C).

2.2. Construction of average molecular structure models

To construct the average molecular structure models of four binders, a series of investigations were conducted including the element composition and structure parameters. A Vario EL-III elemental analyzer was used to examine C, H, N, and S contents. Structure parameters were obtained by improved Brown-Ladner (B-L) methods with proton nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), and Fourier transform infrared spectroscopy (FTIR). According to the results of GPC and element compositions, the chemical formula of the four binders can be determined, as shown in Table 3.

Based on the improved B-L methods, the number of atoms of aromatic carbon, naphthenic carbon, and alkane branched chain carbon was calculated step by step to construct the average molecular structure model of four asphalt binders. The main structure parameters of four binders are listed in Table 4.

The specific construction and verification process will not be repeated in this paper, and more details can be found in the author's subsequent paper. According to Table 4, the average molecular