Fuel 174 (2016) 267–273

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders

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ARTICLE INFO

Article history:
Received 8 November 2015
Received in revised form 29 January 2016
Accepted 5 February 2016
Available online 11 February 2016

Keywords:
Molecular diffusion
Molecular dynamics
Virgin binder
Aged binder
GPC

ABSTRACT

The incorporation of recycled (aged) binder into virgin asphalt has become more popular in asphalt paving industry nowadays. However, the exact mechanism of the diffusion process between virgin and aged binders is still largely unclear. This paper presents a study in which molecular dynamics (MD) simulation was employed to investigate the diffusion between virgin and aged binders. Two asphaltic models with three components including asphaltenes, resin, and oil were built with different components ratio. The model of aged binder was constructed by increasing the asphaltenes ratio on the basis of virgin binder. The results of simulation was verified by GPC and both show that the diffusion of large molecules in asphalt was a critical factor for the diffusion of binders in that it was more susceptible to the changes of temperature. In an inter-diffusion model of virgin and aged binders, the diffusion coefficients of binders were not only determined by the diffusion ability itself, but also influenced by the properties of the diffusion acceptor. Based on this finding, the effect of different sequence of adding rejuvenator during recycling of asphalt mixtures was investigated. The result shows that adding rejuvenator into aged binder first could accelerate the inter-diffusion rate between virgin and aged binder in maximum level, thus increased the efficiency of recycling.

1. Introduction

Asphalt binders act as thermoplastic adhesives for the aggregates in pavement structures. Historically people have been treating the binder as a homogeneous "glue" within the binder aggregate composite. Recently, the use of aged binders including recycled asphalt pavement (RAP) and recycled asphalt shingles (RAS) has become more and more popular, due to environmental and economic concerns. The incorporation of aged or highly aged (such as binder from RAS) asphalt binder into asphalt paving mixtures has raised main questions. There have been concerns over the overall mixture performance with the inclusion of recycled asphalt [1–5] as well as the blending efficiency between virgin and aged binders [6,7]. When RAP/RAS is recycled into asphalt mixtures, one key question is how much of the aged binder in RAP/RAS can be blended into virgin binder. There are three assumptions about the blending situation between virgin and aged binders. The first one is that the aged binder is expected to attain enough workability to blend with virgin binder so as to coat both the virgin and recycled aggregates as a homogeneous film. The second assumption is the "Black rock" theory that is based on the premise that the RAP/RAS may actually perform as nothing more than an aggregate. The third assumption is that partial blending happening between virgin and aged binders. This assumption was supported by many researchers and studies show that most of mixing samples belong to this category [2,4,6–9]. A further analysis into the blending between the aged and virgin binder reveals that even though the binders may be "blended" together, they may still retain their original microstructures and behave as heterogeneous composite, rather than a homogeneous new binder. Nahar et al. [10] and Zhao et al. [11] investigated the microstructures between aged binder from RAP [10] and RAS [11] and the virgin asphalt and concluded that there existed a "blending" zone in which the aged and virgin binders started to co-mingle and formed a homogeneous new binder. However the governing mechanism(s) of blending at the molecular level has not been well instigated.

The blending between virgin and aged binders can be defined as an inter-diffusion process, in which virgin and aged binder diffuse into each other and become homogeneous at molecular level (shown in Fig. 1). The diffusion rate of binders varies under different mixing conditions and thus results in diverse degrees of

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http://dx.doi.org/10.1016/j.fuel.2016.02.022
0016-2361/

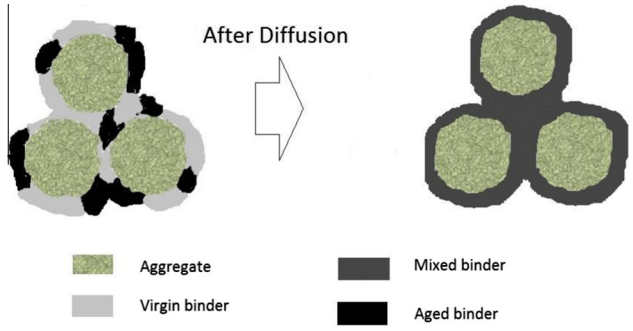

Fig. 1. Diffusion process between virgin and aged binders.

blending at molecular level. Due to the complicated chemical structures of binders and the influencing factors, the mechanism of the diffusion process is difficult to quantify. Therefore, it is still difficult to design an optimized procedure that can maximize the true blending with the proper mixing conditions and addition of additives (such as rejuvenating agents). A better understanding of the asphalt binder diffusion process and correctly quantify the influencing factors will help better utilizing the recycled asphalt materials without compromising the performance of asphalt pavements.

The main objective of this study was to use molecular dynamics (MD) simulation as a tool to simulate the diffusion of virgin and aged binders and investigate the approaches that can accelerate the diffusion rate. Gel permeation chromatography (GPC) was considered to validate the MD model constructed in this study. Utilizing the validated MD model, the molecular diffusion between virgin and aged binder was quantified and the effects on the sequence of adding rejuvenator during asphalt recycling was investigated.

2. Molecular diffusion of asphalt binders

The diffusion process investigated in this study refers to the binder homogenization after virgin and aged binders have contacted to each other. The earlier studies of asphalt diffusion were conducted to evaluate the penetration of rejuvenators into the asphalt [12–15]. The virgin-aged binder diffusion was brought to the attention of researchers in recent years due to the increased use of recycled materials [16–18]. Karlsson et al. [16] used dynamic shear rheometer (DSR) with parallel plates to monitor the diffusion of a soft bitumen (rejuvenator) into a stiff one at 60, 80 and 100 °C. The diffusion coefficients determined were compared with the corresponding diffusion coefficients obtained from FTIR-ATR. The comparison showed that the rate of diffusion detected by the DSR are of the same magnitude, but somewhat higher than the ones detected by FTIR-ATR. Zhao [6] conducted an analysis of diffusion for RAP and RAS mixtures through staged extraction method. The extracted binder was subjected to GPC to obtain large molecule size percentage (LMS%) for further analysis. The results indicate that a relatively complete diffusion process could be achieved at 155 °C within 15 min and 125 °C within an hour in RAP mix. The RAS-virgin binder diffusion is found to be in a very slow rate. The finding suggested that the binder homogeneity caused by molecular diffusion could potentially be an issue for RAS mixtures.

3. MD simulation

3.1. Background on molecular simulation

MD simulation means using statistical mechanics-based theoretical methods and computational techniques to model or mimic the behavior of molecules under different conditions [19,20]. In MD simulation, a model is constructed to represent a molecule and then the atoms within the molecule are assigned a force field that is consistent with. The function of force field is to determine the potential energy of the molecules. The properties of molecular models can be simulated by using a system of coupled nonlinear partial differential equations that are based on Newtonian mechanics. The interactions among molecules are determined by the force field used. In MD simulation, the properties of molecular model such as energy density and diffusion coefficient can be determined at any given point in time.

MD simulation has been commonly used to model the diffusion behavior in polymer molecules. Torres [21] applied molecular simulation to investigate the properties of ultrathin polymeric films near the glass transition and showed that the diffusion coefficient of ultrathin polymeric films depends on the dimensions of the system. Charati [22] calculated the diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 at 300 K in four silicone polymers by MD simulations. The estimated diffusion coefficients are found decreasing with the increasing size of the polymer side chains and of the penetrant molecules. Krishna Pant carried out a simulation of diffusion of a small-molecule penetrant in an amorphous polymer matrix for the examples of methane in polyethylene (PE) and methane in polyisobutylene (PIB). The results are in accord with the available experimental data [23].

The use of molecular simulation to understand the behavior of asphalt binders is still limited. Zhang [24,25] used MD simulation to calculate rotational relaxation time, diffusion coefficient, and zero-shear viscosity for a model asphalt systems over a temperature range of 298–443 K. Two three-component systems are taken as simple computational models of asphalt. In a follow-up work, Zhang [26] investigated the physical properties and microstructures of computational model asphalts using MD simulations in an all-atom framework. A new asphalt model was proposed that is targeted toward asphalt AAA-1 of the Strategic Highway Research Program (SHRP) based on elemental composition and speciation. The density and thermal expansion coefficient matches better with experimental data than the predictions using earlier model asphalts. Bhasin et al. [27] employed MD simulation to investigate the correlation of chain length and chain branching to self-diffusivity of binder molecules. The findings based on molecular simulations are consistent with the experimental data. The results demonstrates a good correlation between the chain length and branching to the healing characteristics of different asphalt binders.

3.2. MD simulation methodology

One commercial software Material Studio was used for simulation in this research. The first step of conducting molecular simulations is to build molecular model. An ensemble of three different types of molecules, each representing one component of asphalt binders (asphaltenes, resin, and oil) was used as asphalt model. This approach followed the method used by Zhang [24–26]. A structure for the asphaltenes molecule that was originally proposed by Groenzin and Mullins [28] was adopted in this research. The *n*-C22 and 1,7-dimethylnapthalene molecules were used to represent resin and oil separately. The chemical structures of three components is shown in Fig. 2. The weight proportion of asphaltenes, resin, and oil for virgin and aged binder was selected as approximately 20-20-60 and 40-20-40, respectively. The concentrations of *n*-C22 and 1, 7-dimethylnapthalene were chosen based on the alkane: aromatic carbon ratio (72.2:27.8) reported by Storm et al. [29] for the oil components, thus treating 1,7-dimethylnapthalene as combing aspects of oil and resin categories. This led to mixtures with 60 wt% *n*-C22 and 20 wt%