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Study on the effect of aging on physical properties of asphalt binder from a microscale perspective

Xin Qu [a,b], Quan Liu [b], Meng Guo [c], Dawei Wang [a,b,d,*], Markus Oeser [b]

[a] School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, PR China
[b] Institute of Highway Engineering, RWTH Aachen University, D52074 Aachen, Germany
[c] College of Architecture and Civil Engineering, Beijing University of Technology, Beijing 100124, PR China
[d] Department of Road and Railway Engineering, Beijing University of Technology, Beijing 100124, PR China

HIGHLIGHTS

- Six molecular models of asphalt binders at different aging states are created.
- Asphalt binder models are optimized according to some chemical test.
- Study on different aging states of asphalt binder on a micro scale.
- Some correlations between micro and macro properties of asphalt binders are proposed.

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ABSTRACT

The asphalt binder in pavement mixtures frequently exposed to oxygen and undergoes daily temperature cycles. This results in oxidation and dehydrogenation of its chemical composition, leading to the aging of the asphalt binder. The aging process of asphalt binder directly affects the pavement's service life and therefore has been subject to intense research regarding the chemical composition and rheological properties. However, the microscopic reasons for these changes are not yet clear. A molecular dynamics (MD) simulation is employed to investigate the aging process from a microscale perspective. Six molecular models for six asphalt binders at different aging states are created based on the ratio of saturates, aromatics, resin and asphaltene (SARA) as well as carbonyl and sulfoxide indexes to investigate the effect of aging on physical properties of asphalt binder have been investigated. The results explain the mechanism for hardening of asphalt binder during aging process, and find some correlations between micro and macro phenomena.

1. Introduction

Oxidation and dehydrogenation occur in the asphalt binder during the aging process. In the processes of mixing, storage, transportation and paving, asphalt binders undergo a series of chemical and physical changes. The original properties are changed gradually, and the material becomes harder and brittle. These changes are called aging [1–3].

It is essential to describe the aging mechanism of asphalt binders from a chemical point of view. So some researchers divided the binder into asphaltene and maltenes. Maltenes can be further subdivided into resins, aromatics and saturates. Many properties of asphalt are determined by the composition and interactions of these fractions. It is generally accepted that the aromatics change into resins which in turn become asphaltene during the aging process, while the saturates essentially remain unchanged, as can be concluded from their low chemical reactivity [4,5]. In addition, aging of asphalt binder leads to an increase of its softening point, a decrease of penetration and ductility, the low temperature performance and fatigue resistance performance of pavements deteriorates significantly. Meanwhile, aging of asphalt binder can also have a positive influence on high temperature performance of pavement [6,7].

Understanding the effects of aging on the physical and chemical properties of asphalt binder is important to allow for tailored design processes and extend the service life of pavement. Lu et al. studied the effect of aging on the chemistry and rheology of seven asphalt binders and observed that aging influences bitumen

* Corresponding author at: Institute of Highway Engineering, RWTH Aachen University, D52074 Aachen, Germany.
E-mail address: wang@isac.rwth-aachen.de (D. Wang).

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chemistry and rheology significantly [8]. Wang et al. studied the surface morphology of five asphalt binders at different aging states using applying the tapping-mode of an atomic force microscope (AFM) and found that certain micromechanical properties are in good correlation with the rheological properties and the asphaltene content as well as the size of microstructures. Both seem to affect the micromechanical properties of the binders [9,10]. Zhang et al. investigated the aging of bituminous mortar using a DSR test and finite element models to study the effects of aging on the complex shear modulus and fatigue resistance [11].

However, the underlying molecular processes of aging and the variety of mechanical properties before and after aging are not clear at present. Little research has been conducted to uncover the aging process of asphalt binders from the molecular level, which is why a molecular dynamics (MD) simulation is selected in this paper to gain new insights and study the effects of aging on physical and chemical properties of asphalt binder. The MD simulation is an effective method to investigate the microstructure and the micro-scale properties of asphalt binder [12–25]. Xu and Wang studied the mean square displacement, radial distribution function and diffusion coefficient of molecules of virgin and aged asphalt binders [20].

In order to create suitable and reliable asphalt binder models for different aging states, the chemical compositions of the asphalt binder at the respective aging states must be identified. It is known that the fractions in asphalt binder change and that the carbonyl and sulfoxide functional groups increase during the aging process [7]. The Corbett separation and Fourier transform infrared (FTIR) spectroscopy are employed to detect the fraction variation as well as the variation of carbonyl and sulfoxide functional groups. The Corbett separation is accomplished with solubility procedures and column chromatographic techniques. Normally, eluents are used in an order from weak to strong polarity, whereafter the fractions are obtained. FTIR is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. The use of FTIR offers quick reliable data regarding aliphaticity, aromaticity and oxygenation rates of the asphalt binder [11]. Because each functional group has its own unique wavelength, the spectrum can accurately characterize the chemical composition of the substance. Hence, FTIR provides valuable chemical information about the molecular bonds and vibrations.

Based on the abovementioned processes, six suitable asphalt binder models are constructed at different aging states, which represent the properties on a molecular scale. Furthermore, the rheological property variations are investigated using Dynamic Shear Rheometer (DSR) test and other micro properties are obtained with MD methods.

The objective of this paper is to create six asphalt binder models for two kinds of asphalt binders from manufacturer Nynas and Dohmen at three aging states. Therefore, molecular models are constructed at different aging states which correspond with the proportions of SARA fractions, carbonyls and sulfoxides. The validation of molecular models is done based on selected thermodynamic properties including density, cohesive energy density and surface free energy. The molecular structures of these six asphalt binders at different aging states are simulated to investigate the correlations between molecular parameters and macro properties of asphalt binder through experimental methods and simulations to identify the aging mechanism on a molecular scale.

2. Materials and methodology

2.1. Materials

#70/100 asphalt binder from the manufacturer Nynas (NY) and #50/70 asphalt binder from the manufacturer Dohmen (DO) are used in this paper, their physical properties are shown in Table 1.

The properties of asphalt binders change due to aging during the service period, which cause changes in the chemical fractions. Therefore, the asphalt binder NY is treated with the Rolling Thin Film Oven Test (RTFOT) [26] and the Pressure Aging Vessel (PAV) test [27] in order to simulate the aging of the asphalt binders during construction and service life. The RTFOT and the RTFOT + PAV test have become the most common methods for simulating short- and long-term aging, respectively. Each version of the asphalt binder is identified (ID) in Table 2.

2.2. Test programs

2.2.1. Corbett separation

The Corbett method has been widely used to separate asphalt binder into saturates, aromatics, resin and asphaltene (SARA) [28]. The process is performed by means of solubility procedures and column chromatographic techniques. The scheme of the Corbett separation process is shown in Fig. 1.

2.2.2. Fourier-transform infrared spectroscopy

The Fourier transform infrared spectrometer (FTIR) has the advantages of high sensitivity, an accurate wave number, quick results, non-invasiveness and good reproducibility. It is an effective means to identify the material and analyze the functional groups; it is commonly used to determine the molecular changes associated with oxidation in asphaltic materials. The FTIR principle is based on the specific vibration and rotation modes of different types of molecular bonds. The latter can be identified by characteristic bands in the absorption spectrum of the transmitted infrared radiation [29,30].

Table 2
The ID of different asphalt binders.

Material	ID	
	NY	DO
Unaged binder	NY1	DO1
Short term aged binder	NY2	DO2
Long term aged binder	NY3	DO3

Table 1
Physical properties of asphalt binder NY and DO.

Tests	Value		Technical requirements	Test method
	NY	DO		
Penetration/0.1 mm	76.47	48.6	70–100/50–70	DIN EN 1426
Softening point/°C	46.4	50.7	≥45	DIN EN 1427
Ductility/cm	≥150	≥150	≥100	DIN EN 52,013
Density/g*cm^{-3}	1.021	1.019	–	DIN EN 12,697