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Effects of aging on the properties of asphalt at the nanoscale

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HIGHLIGHTS

- Oxidative aging increases the spatial variations of asphalt properties at the nanoscale.
- More severely aged asphalt takes longer to recover from micro damages.
- For the same asphalt, moderate aging increases the adhesive/cohesive strength.
- Both asphaltenes content and the size of microstructures play a role in determining asphalt micromechanical properties.

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ABSTRACT

Conventional rheological and chemical tests provide a global view of asphalt property and composition changes upon aging, but offer little details on the changes at the microscopic level. Using atomic force microscopy (AFM), this study analyzed the micromechanical properties of five asphalts with different aging conditions. Rheological and chemical tests were also used to characterize the global properties of the asphalts. Aging was found to significantly increase the spatial variations of the sample properties. It generally increases the ratio between the dissipated energy and total work to deform the sample during the indentation process by AFM probe. It also appears to increase the adhesive and/or cohesive strength of the sample. Certain micromechanical properties and the rheological properties are well related. The asphaltenes content and the size of microstructures both appear to affect the micromechanical properties of the binders. AFM provides a promising addition to the traditional rheological test for asphalts, but more studies are needed to connect the micromechanical properties with performance-related properties.

1. Introduction

As an organic material, asphalt in hot-mix asphalt (HMA) pavement is susceptible to oxidative aging by reacting with atmospheric oxygen [1]. Oxidative aging causes asphalt hardening, which leads to pavement embrittlement and the development of distresses such as cracks or fractures [1]. As a key performance factor in HMA pavement, asphalt aging has received extensive attention for decades [1–3]. Much progress has been made on understanding the fundamental physical–chemical process of asphalt oxidation and the oxidation kinetics [1–4]. In Superpave® specification, asphalt is artificially aged in a rolling-thin film oven (RTFO) to simulate aging that occurs during production and construction and in a pressure aging vessel (PAV) to simulate aging that occurs 5–7 years in the field [5]. Before and after the aging treatments, a suite of tests are conducted to characterize the asphalt binder's rheological properties at different temperatures and loading conditions. In chemical analysis, the numerous types of molecules in asphalt are generally separated into four fractions [6]: saturates, naphthene aromatics (NAs), polar aromatics (PAs), and asphaltenes. Upon oxidation, PAs transform to asphaltenes, whereas NAs first transform to PAs and then to asphaltenes [6,7]. The increase in asphaltenes has been shown to be related to the increase in asphalt viscosity [8,9]. Chemical changes have also been examined through the changes in oxygen-containing functional groups in asphalt, in particular the carbonyl and sulfoxide functional groups [1,10]. Laboratory tests revealed a linear correlation between the increase of log viscosity and carbonyl formation during asphalt oxidation [8,11,12].

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The conventional physical and chemical tests provide a global view of the asphalt properties and compositions. However, they offer little details at the microscopic level, where asphalt reveals itself as a colloidal system in which micelles are dispersed in an oily medium [13]. It remains a question how asphalt properties vary spatially at the nanoscale and how such variations change with aging state. It is also unclear if there is any relationship between the properties measured at the microscopic level and global rheological behaviors. Such knowledge is not only beneficial in understanding the fundamental asphalt aging mechanisms, but also may potentially assist practical applications including asphalt material selection, recycling, and rejuvenation.

Recently, atomic force microscopy (AFM) has been used to study the morphology [e.g., 14–16] and micromechanical properties of asphalt [e.g., 17–19]. However, the use of this technique to study the change in micromechanical properties of asphalt due to aging is still lacking. The study as presented in this paper aims to identify the changes in the magnitude and variation of the micromechanical properties of asphalts with different aging states. The rheological properties of the asphalts were obtained using a dynamic shear rheometer (DSR), and their chemical properties were characterized by Corbett fraction and Gel Permeation Chromatography (GPC). The relationships between the micromechanical properties and the rheological/chemical properties were also examined.

2. Experiments

2.1. Samples and test equipment

Three types of paving grade asphalt in Hong Kong were used. The first asphalt is a pen 60/70 binder. It was treated in RTFO at 163 °C for 85 min, followed by PAV treatment at 100 °C for 20 h. Both the original binder and those after simulated short-term and long-term aging were used for study. The second asphalt was extracted and recovered from the wearing course (WC) of a road pavement after 7 years of construction. The original binder used is pen 60/70. An open-graded friction course (OGFC) was placed on the top of the WC; therefore, asphalt aging in the WC was not affected by direct sunlight. The third asphalt was extracted and recovered from the road base (RB) layer of a heavily trafficked 36 year-old road pavement. The original binder grade is pen 80/100, with reported penetration value of 83 for the unaged binder and 57 for the binder after being treated in thin film oven (TFO) [20]. The binder extraction and recovery processes followed the ASTM standard ASTM D2172/D2172M-11 [21] and European Standard EN 12697-3:2005 [22], respectively. The five binders, with presumably wide differences in aging states, were used for subsequent analysis.

Corbett fractions were used to separate each binder into four components: saturates, NAs, PAs, and asphaltenes in accordance with the Chinese standard NB/SH/T0509-2010 [23]. Waters Gel Permeation Chromatography (GPC) equipped with 1515 isocratic HPLC pump and 2414 refractometer detector were used for chromatographic analysis. A series of two columns (Styragel Column HR3 and HR4) were used for identifying the distributions in molecular weight. Tetrahydrofuran (THF) was used as the mobile phase in GPC analysis and the flow rate was controlled at 1 mL/min. For each test, about 100 mg asphalt binder was dissolved into 10 ml THF at the room temperature. The solution was filtered by using a 0.22 μm membrane prior to being injected into the columns. The volume of each specimen injected into the system was 25 μL and duplicate specimens were tested for each sample. The rheological properties of the asphalts were tested using a DSR. For the non-aged and laboratory-aged asphalt samples, test frequency ranged from 10^{-3} to 10^{2} Hz at preset temperature levels. A lengthy test was conducted across the frequency range so that time–temperature superposition was not needed for the construction of master curves. For the WC and RB samples, test frequency ranged from 10^{-1} to 30 Hz at preset temperature levels and time–temperature superposition was used for building the master curves of the complex shear modulus $|G^*|$ and phase angle δ. The tests were conducted under the controlled stress mode and the strain levels were chosen to be within the linear viscoelastic range.

A Bruker AFM with NanoScope® 8 controller was used for the AFM tests. AFM may be operated in different modes, including tapping, contact, and non-contact. In tapping mode, the probe tip of AFM only contacts the sample surface intermittently, while in contact mode, the probe tip indents the sample surface. In the study, tapping mode was used to examine the surface morphologies and phase contrasts of the specimens while contact mode was used to obtain force–displacement (FD) curves. Two types of probes were used in the study. For tapping mode, the probe is made of Si, N-type (AppNano, model ACTA). The size of the cantilever is 125 μm long, 30 μm wide, and 4 μm thick. The tip radius is less than 10 nm and its height is between 14 and 16 μm. The resonance frequency is between 200 and 400 kHz and the spring constant ranges from 13 to 77 N/m. For contact mode, more sensitive probes were used. The probes were made from the same manufacturer, with the cantilever size of 225 μm long, 43 μm wide and 1 μm thick. The tip radius is 7 nm and its resonance frequency is between 18 and 38 kHz. The spring constant is between 0.02 and 0.18 N/m, which is much less than the spring constant of the tapping-mode probe.

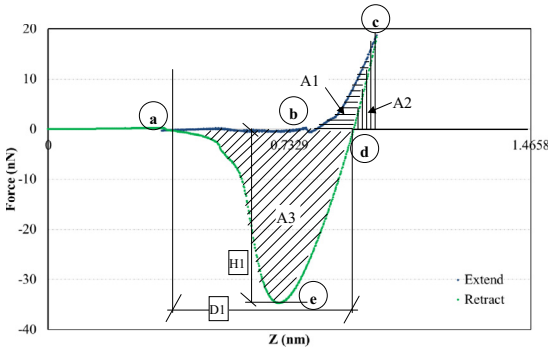

Fig. 1. An example of the AFM force–displacement (FD) curve.

The actual spring constants of the probes used for contact mode were determined by the thermal-tune method whenever the probe was installed [24]. The spring constant of the probe used for the non-aged and RTFO-aged binders was determined to be 0.174 N/m, while the spring constant of the probe used for the PAV-aged, extracted binder from wearing course (WC) (7 years old), and extracted binder from road base (RB) course (36 years old) was 0.1533 N/m.

The AFM specimens were prepared by dissolving 1.0 g of asphalt samples in 50 mL of dichloromethane. The solution was spin cast onto a mica sheet, which was used as the microscope slide. The spin-cast samples were left in the air for 24 h before the test for the evaporation of the solvent. The film thickness, measured by surface profiler, ranges from 1.3 μm to 3.5 μm. In addition, a heat lamp was used to drive off the residual solution and surface moisture prior to the test. The experiment was conducted in a controlled environment of constant 24 °C and 71% humidity. It is believed that the environmental effects on all the asphalt specimens were the same hence they did not affect the relative comparisons between the specimens. The maximum compressive force used to indent the sample was kept about 20 nN and the drive speed was about 3 μm/s.

2.2. Parameters obtained from the FD curves

About 30 FD curves were obtained from each sample at random locations. A typical curve obtained from the extracted WC binder is shown in Fig. 1, where the "Extend" line depicts the probe's approach to and penetration into the specimen while the "Retract" line represents the probe's retraction from the specimen. In the figure, A1 measures the energy to deform and dissipate into the sample during the indentation process [25], while A1 + A2 measures the total work done on the cantilever and the sample. A1 + A2 provides an indication of the magnitude of energy used to deform the sample during the indentation. A plasticity index (PI) has been defined as [25]:

$$PI = \frac{A1}{A1 + A2} \quad (1)$$

An ideal elastic material would result in A1 = 0 and PI = 0 while an ideal plastic material would result in A2 = 0 and PI = 1 [25]. A3 measures the work during the "pull-off" cycle, which indicates the energy required to break the contact between the sample and probe tip [19]. "H1" in Fig. 1 represents the maximum force to break the adherence between the sample and probe tip (or cohesion within the sample) and "D1" is the travel distance of the probe tip from zero displacement to the end of the "pull-off" cycle. The corresponding positions and deflections of the probe are shown in Fig. 2.

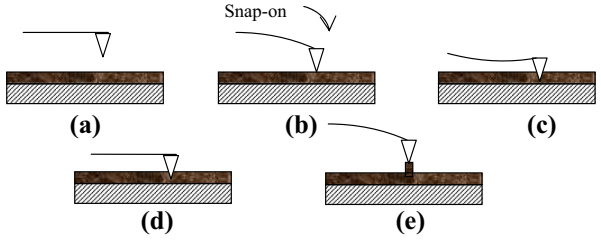

Fig. 2. The configuration of cantilever and tip corresponding to the positions shown in Fig. 1.