Rheological, microscopic, and chemical characterization of the rejuvenating effect on asphalt binders

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HIGHLIGHTS

• The rejuvenating effect for aged binders was thoroughly evaluated at both macro- and micro-scales.
• Results suggest that changes in chemical compositions contributed to mechanical properties variations.
• Characterization of the rejuvenating effect benefits the effort for better recycling bituminous materials.

ABSTRACT

With the increasing environmental awareness and rising costs of virgin binders, reclaimed asphalt pavement (RAP) has been used as an alternative for energy and cost saving in asphalt pavements. However, RAP binders have been aged to different extents during pavements’ service life and adding rejuvenating agents provides a practical means for restoring the mechanical properties of the aged binders reducing the needed additional virgin binder. In many studies, the rejuvenating effect has been evaluated in terms of the improvement of rejuvenated binders’ rheological properties whereas the fundamental rejuvenation mechanism remains unclear. In this research, two different asphalt binders from the Materials Reference Library of the Strategic Highway Research Program (SHRP) were aged, and rejuvenated by complete blending with two commonly used rejuvenators. The rheological properties of the virgin, aged, and rejuvenated binders were tested using the dynamic shear rheometer and the bending beam rheometer. Furthermore, in order to better understand the rejuvenating effect, surface microscopic properties and chemical composition of the binders were measured using atomic force microscopy (AFM) and SARA (Saturates, Aromatics, Resins, Asphaltenes) fractionation, respectively. Results indicated that the bulk mechanical properties (complex modulus and viscosity) of the rejuvenated binders were in between those of the virgin and aged binders. Aging and rejuvenation led to morphological changes as compared to their virgin binders; however, the rejuvenated binders did not always reproduce the microstructures of the virgin binders. Microscopic measurements on adhesion and dissipation of virgin, aged, and rejuvenated samples were qualitatively consistent with the bulk rheological results. SARA separation results suggested that changes in chemical fractions were responsible for the stiffening effect of aging and the improvement of mechanical properties with the addition of the rejuvenators. Such a systematic approach of characterizing the rejuvenating mechanism will benefit the effort of producing more sustainable RAP-containing asphalt pavements.

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1. Introduction

As of 2011, more than 40 state agencies in the US allow to use above 30% reclaimed asphalt pavement (RAP) in mix design of Hot Mix Asphalt (HMA) [1], however, currently the average RAP use is still between 10% and 20% [2]. According to the Superpave mix design specification (AASHTO M 323), when more than 15% RAP is used in the mix design, it is required to reduce the binder performance grade (PG) by one to compensate for the aged RAP binder. Furthermore, when adding more than 25% RAP, virgin binder PG has to be determined based on the properties of extracted RAP binder. Such requirements are set to ensure that the virgin binder compensates for the deteriorated mechanical properties of the
RAP binder in order to avoid cracking failures in the asphalt pavement. However, this also leads to additional expenses for contractors in terms of purchasing unconventional binder grade, installing additional hot storage tanks, maintaining a laboratory with extraction and testing equipments or outsourcing of the required additional testing. In many cases, this discourages the contractors to produce high RAP content mixtures because the savings from a relatively small increase in RAP content are outweighed by the increased expenses.

The use of rejuvenators (i.e., products that are used for restoring the mechanical properties of aged binders) is a relatively poorly understood alternative for mix design of RAP-containing HMA. This is primarily due to concerns associated with their ability to diffuse in the RAP binder and to provide the required long term performance for another service period of the pavements [3]. However, introducing rejuvenators provides major benefits as compared to merely bumping the virgin binder grade as follows:

- Unrestricted RAP content using a single rejuvenator;
- Cheap storage, since in most cases rejuvenators do not require heating;
- Simple addition to the mixture using volumetric pump or existing liquid additive dosage system;
- Ability to add the precise required dose based on the RAP binder properties.

These advantages would help increase the average amount of RAP used in HMA asphalt pavements if the rejuvenating mechanism is better understood. Previous studies suggest that rejuvenators should replenish the volatiles and light chemical fractions that have been lost during aging of pavements [4] by providing a homogeneous system where asphaltenes are well dissolved and prevented from precipitation or flocculation [5]. Other research has shown that a better rejuvenating effect can be attained with high amounts of resin or aromatic fractions [6]. However, a systematic approach of exploring how the rejuvenator modifies the chemical, microscopic and mechanical properties of the aged asphalt binders is still absent.

In this study, two virgin asphalt binders from different crude sources were aged using both Rolling Thin Film Oven (RTFOT) and Pressurized Aging Vessel (PAV) methods. In order to verify the capability of rejuvenators to restore the mechanical properties of the aged binders, two different rejuvenators were added into the aged binders. For better understanding of the rejuvenating mechanism at both macro and micro scales, rheology, surface microscopic properties, as well as chemical fractions of the virgin, aged and rejuvenated asphalt binders were characterized using dynamic shear rheometer (DSR), bending beam rheometer (BBR), atomic force microscopy (AFM), and SARA (Saturates, Aromatics, Resins, Asphaltenes) fractionation.

2. Materials and methods

2.1. Materials

2.1.1. Virgin asphalt binders

Two types of asphalt binders, AAD (PG 58–28) and ABD (PG 58–10), were obtained from the Materials Reference Library of the Strategic Highway Research Program (SHRP). They were chosen because of variations in their crude source, SARA fractions, chemical elemental analysis, physical and mechanical properties, as indicated in Tables 1 and 2. Between the two virgin binders, AAD is a “softer” binder with a higher wax content and higher asphaltene content in comparison to ABD.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Crude source, SARA fractions, and elemental analysis of the asphalt binders according to reference [7].</td>
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<tr>
<td>Binder</td>
</tr>
<tr>
<td>AAD (PG 58–28)</td>
</tr>
<tr>
<td>Saturates</td>
</tr>
<tr>
<td>Aromatics</td>
</tr>
<tr>
<td>Resins</td>
</tr>
<tr>
<td>Asphaltenes</td>
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<tr>
<td>Hydrogen</td>
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<td>Oxygen</td>
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<tr>
<td>Vanadium</td>
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<tr>
<td>Nickel</td>
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<tr>
<td>Iron</td>
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<tr>
<td>1.94</td>
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</tbody>
</table>

2.1.2. Rejuvenators

Two generic rejuvenators, aromatic extract and waste vegetable oil (WV oil), were used in the study. Table 2 shows their viscosity and specific gravity measured by the authors and other relevant properties obtained from the manufacturers. A brief description of the two rejuvenators is also provided below. Based on previous studies [8,9], 12 wt.% of each rejuvenator was added to the binders.

Aromatic extract is a traditional rejuvenator with dominant polar aromatic molecules. According to the manufacturer, aromatic extract contains approximately 75% of aromatic oil and resin compounds with small amount of saturate oil. Chemical compositions of the aromatic extract were determined in this study using SARA fractionation and discussed later (Section 3.3).

WV oil is increasingly used for bio-diesel production. It is derived from fast and convenient food frying oil and also referred to as “yellow grease”. This product usually has low free fatty acid content (<15%), and MIU (Moisture, Impurities, Unsaponifiables) (<2%) [11]. According to the manufacturer, WV oil used in this study consists predominately of peanut, sunflower, and canola oils, with large concentrations of oleic and linolic acids.

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Physical and viscoelastic properties of the asphalt binders [7].</td>
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<tr>
<td>Aging state</td>
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<tr>
<td>Unaged</td>
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<tr>
<td>Viscosity at 60°C</td>
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<tr>
<td>Penetration at 25°C</td>
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<tr>
<td>Softening point</td>
</tr>
<tr>
<td>G’</td>
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<tr>
<td>RFTO residue</td>
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<td>G’</td>
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<tr>
<td>PAV residue</td>
</tr>
<tr>
<td>G’</td>
</tr>
<tr>
<td>Stiffness at –10°C</td>
</tr>
<tr>
<td>m-value at –10°C</td>
</tr>
</tbody>
</table>

\* Data are not available.

2.2. Methods

2.2.1. Binder aging

The two virgin asphalt binders were aged using both Rolling Thin Film Oven (ASTM D2872-2004) and Pressurized Aging Vessel (ASTM D652-2008) methods. The combined aging procedures are expected to simulate the field aging of asphalt binders at later stages of pavement life when asphalt has to be removed and needs
treatment (i.e., rejuvenation) before application for another service period.

2.2.2. Addition of rejuvenators

The aged binders were dosed in containers at room temperature, thereafter heated at 145 °C for 40 min and blended for 5 min with 12 wt.% of each rejuvenator by hand. The samples were immediately re-heated for 10 min to remove the air bubbles, blended again for another 2 min, and thereafter left to cool at room temperature. Each blend was then re-heated at 140 °C for 30 min before sampling into containers suited for each test.

2.2.3. Dynamic shear rheometer (DSR) measurements

The rheological properties of virgin, aged, and rejuvenated asphalt binders were measured using a DSR (Anton Paar Physica MCR 301). According to AASHTO T 315, an 8 mm plate-plate geometry with 2 mm gap in strain controlled mode was used. The tests were performed at 40, 50, 60, 70, and 80 °C and frequencies of 0.1–20 Hz at each temperature. These results were shifted to a reference temperature of 40 °C using the time–temperature superposition principle to construct master curves of complex modulus (\(G'\)) and phase angle (\(\delta\)). Shift factors were computed using Williams–Landel–Ferry (WLF) Eq. (1) and a sigmoidal function defined by Eq. (2) was used for fitting the shifted shear modulus data. Larger values of \(G'\) correspond to stiffer asphalt binders, and larger values of \(\delta\) correspond to larger viscous component of the complex modulus. Interpretation of master curves allows to describe the temperature dependence of the viscoelastic behavior of the binder.

\[
\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \tag{1}
\]

\[
\log (G') = \delta + \frac{\alpha}{1 + e^{\frac{T_r - T}{\log a_T - \log e}}} \tag{2}
\]

where,

- \(a_T\) – horizontal shift factor at temperature \(T\)
- \(T\) – test temperature, °C
- \(T_r\) – reference temperature, °C (40 °C in this study)
- \(f\) – testing frequency, rad/s
- \(\delta, \alpha, \beta, \gamma, C_1, C_2\) – fitting parameters determined using least squares method.

2.2.4. Bending beam rheometer (BBR) measurements

BBR tests (AASHTO T 313) were performed for all samples in order to characterize the low temperature cracking potential (i.e., the creep stiffness and creep rate). To increase the resistance to thermal cracking, a lower stiffness is favorable to lessen the thermal stresses developed in the pavements and a high creep rate (also called \(m\)-value) is desirable to rapidly disperse the accumulated stress. Superpave specifications require a maximum stiffness of 300 MPa and a minimum \(m\)-value of 0.3 at the specified test temperature. The minimum pavement design temperature is defined to be 10 °C lower than the test temperature. In this study, a single test temperature of −18 °C was chosen to allow direct comparison of all samples under the same conditions. This temperature would correspond to Superpave low PG of the AAD binder (−28 °C) but is much lower than the PG of the ABD binder (−10 °C). For each sample, the average values of creep stiffness and creep rate from two repetitive tests are reported.

2.2.5. Atomic force microscopy (AFM) measurements

With a sharp tip attached at the free end of a cantilever probe, the specimen surface, AFM is able to measure the materials’ surface morphology and mechanical properties with high resolution. Through microscopic investigations on how the rejuvenator interacts and modifies the aged binders at the micro scale, AFM characterization can provide complementary information on the rejuvenation mechanism of aged binders.

Thin films of asphalt binders were prepared by heat-cast method, which maintains binders’ solid-state microstructure [12]. For morphological measurements, a bead of binder (ca. 50 mg) was dropped onto a glass slide, which was heated for ~2 min in an oven at ~115 °C. Once the binder became liquid, it was spread out with a blade (buttering) to form a thin film. This hot film was left undisturbed for an additional 10 min to allow the surface to flow to a smooth finish. For surface mechanical property measurements that were conducted in a different laboratory using a different AFM, bitumen (ca. 10 mg) was spread over a 0.9 × 0.9 mm² area of a glass slide and the samples were placed in the oven at 110 ± 2 °C for ~20 min. The film was then covered to prevent dust pick-up and left to cool in air to room temperature (~20 °C), and stored for a minimum of 24 h before imaging.

Asphalt binders’ morphology was characterized using an Asylum Research AFM (MFP-3D) with intermittent-contact mode as it minimizes the possible tip contamination caused by binders’ adhesiveness [13]. Budget Sensors silicon tips Tap300AI-G (nominal resonant frequency of 300 kHz and nominal stiffness of 40 N/m) were used for morphological measurements. Tip geometry and stiffness were calibrated using a reference sample (TGT 01, MicroMasch) and a thermal tune procedure, respectively. Asphalt binders’ mechanical properties were measured using a Bruker AFM (MultiMode 8) with a Nanoscope V controller in peak force tapping quantitative nanomechanical (PFT QNM) mode. The data was collected using Nanoscope 8.15. Bruker Tap150A tips (nominal resonant frequency of 150 kHz and nominal stiffness of 5 N/m) were used. The tip radius was calibrated using the Bruker PS-LDPE reference and set as 20 nm. The peak force was set as 15 nN, the feedback gain was 20, and the scan rate was 0.5 Hz. The peak force amplitude and peak force frequency were set as 150 nm and 2 kHz, respectively. Scans of the topographical and mechanical properties were recorded over 40 × 40 μm² or 20 × 20 μm² area with 256 × 256 pixels, depending on the sizes of their specific microstructures. All measurements were conducted at room temperature (~20 °C).

PFT QNM mode is a technique recently developed by Bruker, and it allows simultaneous capture of topographical and mechanical properties by recording instantaneous force curves as the AFM probe approaches and retracts from the sample surface as shown in Fig. 1. As the AFM tip approaches the surface, it experiences an attractive force which causes the tip to jump into contact with the sample. After contact, repulsive forces dominate the tip-sample interaction, leading to a peak force point in the approaching curve. As the tip is retracted, it goes through a minimum force corresponding to the adhesion force and, finally, the contact breaks apart. In PFT QNM mode, the peak force and the indentation depth can be controlled. The surface mechanical properties of asphalt...
binders (i.e., adhesion, dissipation energy, and elastic modulus) are extracted from force curves that are acquired at each pixel of an image and, therefore, a map of each mechanical property is obtained. The adhesion force, also called pull-off force, corresponds to the lowest point of the retraction curve. Dissipation energy is defined as the area between the approach and retraction curve, which is related to a material's damping property. To obtain a material's elastic modulus, a portion of the retraction curve (i.e., 30–90% from the adhesion force to the maximum peak force, corresponding to the linear portion of the curve (Fig. 1)) can be fitted using different contact mechanics models (e.g., Hertz [14], Derjaguin–Müller–Toporov (DMT [15]), JKR (Johnson–Kendall–Roberts [16], and Maugis [17]). Among these contact mechanics, the Hertz model does not consider adhesion; DMT is appropriate for stiff materials with low adhesion; JKR provides good prediction for large tip radii and compliant samples with high surface forces. The Maugis mechanics proposes a parameter lambda, λ, defined in Eq. (3), to characterize a wide spectrum of materials: large lambda (λ → ∞) is for the more compliant, adhesive combinations, approaching JKR mechanics, and for small lambda (λ → 0), the tip-sample system responds like the DMT mechanics.

\[
\lambda = \frac{2.06}{\zeta_0} \left( \frac{R_0^2}{\pi E^2} \right)^{1/3}
\]

where \(\zeta_0\) is the interatomic spacing of the tip-sample system, \(R\) is the effective radius of curvature of the tip-sample system, \(\zeta\) is the work of adhesion, and \(E\) is the reduced elastic modulus, defined as \(E = \frac{1 + \nu^2}{\nu}(1 - 2\nu)\frac{E_t}{E_s}\), in which \(\nu\) is the Poisson’s ratio, and the subscripts \(t\) and \(s\) refer to the tip and sample, respectively. For the tip-binder system, using the relative parameters from the available literature (\(\zeta_0, R, \zeta\) and \(K\) to be 3 Å, 10 nm, 60 mJ/m², and 890 MPa, respectively), the value for \(\lambda\) is calculated to be about 10, large enough indicating that JKR might be more suitable for capturing the tip-binder contact mechanics. However, PFT QNM adopts the DMT model rather than the JKR for real-time modulus mapping of a material, which simplifies the calculation of modulus but may lead to discrepancies that should be noted. The DMT contact mechanics model is shown in Eq. (4).

\[
F - F_{\text{adhesion}} = \frac{4}{3}E \sqrt[4]{R_0^3}
\]

where \(F\) is the instantaneous force on the tip, \(F_{\text{adhesion}}\) is the adhesion force, \(E\) and \(R\) are the same as in Eq. (3), and \(\delta\) is the tip-sample indentation depth.

2.2.6. SARA fractionation

SARA (saturates, aromatics, resins, asphaltenes) fractionation is a frequently used technique for chemical compositional analysis of asphalt binders from different crude sources and binders subjected to various treatments [18]. Resins are sometimes referred as polar aromatics while aromatics as naphthenic aromatics [19]. In this study, SARA fractionation was conducted according to the standard ASTM D4124-09 2010. Asphaltens and maltenes were separated using isooctane (2,2,4-trimethyl pentane, HPLC grade, Fisher Scientific, Waltham, MA, USA). The precipitating solvent was added to the binder sample at a ratio of 40:1 by mass, and the mixture was stirred overnight at room temperature. The sample solution was then filtered through both a Fischer brand filter paper Q2 (pore size 1–5 μm) and a Millipore cellulose ester membrane (pore size 0.22 μm). The asphaltens retained on the filter paper were washed with additional solvent until the filtrate was colorless and dried in a fume hood until a constant weight was obtained. The maltene fraction was recovered by roto-evaporation and dried to a constant weight. Separation of the maltene into saturates, aromatics and resins was carried out by injecting the solution (1 g of the maltene dissolved into 10 ml of n-heptane) into a 70-cm long, 105-cm diameter glass LC (liquid chromatography) column with approximately 100 g of chromatographic grade activated alumina (80–200 mesh, VMR International, US). The three fractions were eluted by introducing the following solvents (all by Fisher Scientific) into the column: 50 ml n-heptane (HPLC grade), 100 ml of toluene (HPLC grade), 75 ml of methanol (HPLC grade)/toluene (50:50 v/v) and 150 ml trichloroethylene (ACS grade). Saturates were collected prior to elution of a fluorescent band migrating up the column. Aromatics characterized by the fluorescent band were collected prior to a dark band migrating up the column below the fluorescent band. Trichloroethylene was finally introduced to strip the column of any remaining ‘dark band’ material defined as the polar aromatics fraction. Fractions were recovered by roto-evaporation and dried to a constant weight.

2.2.7. Test plan

The testing matrix is shown in Table 4. WV oil rejuvenated AAD sample was too soft to complete DSR successfully in the temperature range of 40–80 °C as well as the BBR test at ~18 °C. SARA fractionation was performed on the virgin, aged, and aromatic extract rejuvenated samples for both binders and also the aromatic extract alone. Microscopic morphologies of virgin, aged, and rejuvenated binders were obtained successfully with intermittent-contact mode AFM. Furthermore, preliminary measurements of surface mechanical properties on AAD-based samples faced technical challenges such as tip contamination, excessive deformation under a relatively small compressive force and complicated tip-sample interaction due to the dominant ‘bee-structures’ on the sample surfaces (as shown in Fig. 3). WV oil rejuvenated ABD sample was too compliant under a compressive force that was used for other ABD-based binders. Therefore, AFM mechanical measurements were only carried out for virgin, aged, and aromatic extract rejuvenated ABD samples.

3. Results and discussion

3.1. Rheology

3.1.1. Properties at intermediate and high temperatures

The rheological properties of the virgin, aged, and rejuvenated asphalt binders at intermediate and high temperatures obtained from DSR are shown in Fig. 2. Virgin ABD was stiffer (higher complex modulus) yet more viscous (larger phase angle) than virgin AAD as shown in the master
curves, which supports the results in the SHRP report (Table 2) [7]. For both binders, aging resulted in an increase of the complex modulus and a decrease of the phase angle (corresponding to a lower complex viscosity), which conforms with the well-known aging effect [20,21]. The addition of the rejuvenators into the aged samples decreased the complex modulus and increased the phase angle in comparison to aged samples, to different extents depending on both the binders' crude sources and the rejuvenating agents.

Comparing the effect of the two rejuvenators on one type of binder (ABD), adding 12 wt.% of aromatic extract into the aged ABD binder restored the complex modulus to the level of the virgin ABD and the phase angle in between the virgin and aged samples. Whereas the same dosage of WV oil reduced the complex modulus below the virgin level and increased the phase angle above the virgin level, which are not necessarily desirable features. In this respect, 12 wt.% of aromatic extract achieved the desired level of rejuvenation on this binder compared to the same dosage of the WV oil. These results show that in the case of complete blending, the restoration of rheological properties can be achieved using rejuvenators, the extent of which is binder source and rejuvenator dependent.

The rejuvenating efficiency of 12 wt.% of aromatic extract on the two binders (AAD and ABD) in terms of restoring their rheological properties was similar. For both binders, the complex modulus
master curves for the rejuvenated binders almost overlapped with their source virgin binders. Values of the phase angle for the rejuvenated binders fell in between the virgin and aged samples. However, aging and rejuvenation caused more significant shift of phase angle for AAD-based samples than ABD-based binders at lower frequencies (corresponding to higher temperature). This

Fig. 3. Topographic images of virgin (top row), aged (2nd row), aromatic extract (3rd row), and WV oil rejuvenated (4th row) ABD (left, 20 × 20 µm²) and AAD (right, 40 × 40 µm²) measured at room temperature (~20 °C). The color scales range over 10 nm and 60 nm for ABD and AAD based samples, respectively.
can be attributed to the rheological differences of the two binders from different crude sources.

3.1.2. Properties at low temperature

The BBR results of the virgin, aged, and rejuvenated asphalt binders at −18 °C are reported in Table 5. In accordance with their PG grades, the virgin ABD binder (PG −10°C) is much stiffer and has a lower m-value compared to AAD (PG −28°C). As expected, aging increased stiffness while reducing m-value for both binders; the introduction of the rejuvenators reversed this trend to a certain degree.

Considering the ABD binder, consistent with the observations at intermediate and high temperatures discussed in the previous section, WV oil was more effective in softening the binder compared to aromatic extract. It produced a binder that was significantly softer than the virgin ABD and in fact would pass the Superpave requirement for PG −28°C (Superpave grade is 10°C lower than the test temperature). Aromatic extract softened the aged ABD binder to a level below that of the original virgin ABD, while its rejuvenation effect on aged AAD binder was different with a stiffness slightly higher and an m-value slightly lower than those of the virgin binder. This is somewhat different from the observations at intermediate and high temperatures where the effect of aromatic extract was qualitatively similar for both types of binders. The dependence of the rejuvenating effect of aromatic extract on binder type and test temperature is probably related to the chemical variations between their crude sources.

3.2. Microscopic morphology and mechanical properties using AFM

DSR and BBR tests indicated that when completely blended, the rejuvenators were capable of restoring the rheological properties of the aged binders close to the level of their source virgin binders. In order to better understand the rejuvenating mechanism, surface microscopic morphology and mechanical properties characterization using AFM was carried out.

3.2.1. Microscopic morphology

Microstructures of the virgin, aged, and rejuvenated AAD and ABD samples are shown in Fig. 3. Scan sizes for AAD- and ABD-based samples are different and related to the sizes of their characteristic microstructures. The grayscales for each binder were set to be the same for easy visual comparison among the samples under different treatments.

As shown in the top row in Fig. 3, the two virgin binders displayed considerably different morphologies, even though both of them contain dispersed and continuous domains. Virgin ABD has a dispersed phase with flake-like structures (with an average size of less than 2 μm in diameter) spreading over a smooth matrix phase; whereas elliptical domains containing the “bee-structures” (with major and minor axes of a few microns) dominate the surface of the virgin AAD. The appearance of the “bee-structures” has recently been attributed to the interaction between crystallizing waxes and the remaining non-wax asphalt components [22,23]. The morphological difference between the two binders can be related to their chemical compositional differences as shown in Table 1, most notably the higher wax content of the AAD binder. Furthermore, as noted by Allen et al. [24] the complicated molecular interactions among the various chemical components manifests themselves into the formation of the microstructures.

The effect of aging on the two binders can be seen in the second row in Fig. 3. Upon aging, the size of the flake-like microstructures in ABD decreased while the quantity increased, and it appeared that the large-sized flakes in the virgin binder were replaced by smaller ones after aging. On the other hand, “bee-structures” still appear on the surface of the aged AAD binders, and morphological changes between virgin and aged AAD binder were less obvious compared to the ABD-based binders.

Introduction of the aromatic extract into the aged ABD binder (the third row in Fig. 3) produced dispersed elliptical domains, with “bee-structures” at the center of the domains. This is a similar effect as Pauli et al. observed for the wax-doped binder samples [22]. The aromatic extract is a petroleum-derived rejuvenating agent, and its chemistry supposes to be close to that of the malthene fractions in asphalt binders. Therefore, the mechanism responsible for the formation of the “bee-structures” might occur during the rejuvenation process. The aromatic extract rejuvenated AAD sample exhibited finer-sized “bee-structures” and the amplitude of the undulated “bee-structures” was smaller than that of the virgin and aged ones as indicated by the less noticeable contrast between the ‘bee-structures’ and the matrix. The introduction of the WV oil into the aged binders (both AAD and ABD) did not modify their morphologies significantly, as compared to the aged samples (the fourth row in Fig. 3).

In summary, the addition of the rejuvenators resulted in more significant morphological changes than the aging effect; however, the rejuvenated blends did not always reproduce the microstructures as exhibited on the surfaces of the virgin binders. In addition, the aromatic extract had a stronger impact on the microstructural properties of the binders than the WV oil. The development of asphalt binders’ microstructures depends on the binders’ chemistry and the complicated molecular interactions among the different chemical components and any additives [22]. This helps explain the different surface morphological properties in the binder-rejuvenator combinations examined here.

### Table 5

BBR results at −18 °C for the virgin, aged, and rejuvenated asphalt binders AAD and ABD.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ABD binder</th>
<th>AAD binder</th>
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<tbody>
<tr>
<td></td>
<td>Virgin</td>
<td>Aged</td>
</tr>
<tr>
<td>Creep stiffness (MPa)</td>
<td>760</td>
<td>839</td>
</tr>
<tr>
<td>m-value</td>
<td>0.205</td>
<td>0.159</td>
</tr>
</tbody>
</table>

3.2.2. Microscopic mechanical properties of ABD-based binders

The surface mechanical properties of ABD based binders were measured using PFT QNM mode to further explore the physico-chemical mechanism responsible for the rejuvenation process. Results of the mechanical properties for virgin, aged, and aromatic extract rejuvenated ABD samples are shown in Fig. 4. The grayscale for each of the properties were set to be the same for easy visual comparison among the different samples. Maps of the different mechanical properties (adhesion, dissipation, and DMT modulus) for the virgin, aged and rejuvenated samples (Fig. 4) consist of similar patterns as those from AFM intermittent-contact mode (Fig. 3). These results indicate that morphological characterization for these samples was repeatable and that complete blending between the binder and the rejuvenator was achieved. The minor differences between morphological properties acquired from these two modes might result from variance during sample preparation (Section 2.2.5), namely the amount of binder and annealing procedure.

As shown in the top row in Fig. 3, the two virgin binders displayed considerably different morphologies, even though both of them contain dispersed and continuous domains. Virgin ABD has a dispersed phase with flake-like structures (with an average size of less than 2 μm in diameter) spreading over a smooth matrix phase; whereas elliptical domains containing the “bee-structures” (with major and minor axes of a few microns) dominate the surface of the virgin AAD. The appearance of the “bee-structures” has recently been attributed to the interaction between crystallizing waxes and the remaining non-wax asphalt components [22,23]. The morphological difference between the two binders can be related to their chemical compositional differences as shown in Table 1, most notably the higher wax content of the AAD binder. Furthermore, as noted by Allen et al. [24] the complicated molecular interactions among the various chemical components manifests themselves into the formation of the microstructures.

The effect of aging on the two binders can be seen in the second row in Fig. 3. Upon aging, the size of the flake-like microstructures in ABD decreased while the quantity increased, and it appeared that the large-sized flakes in the virgin binder were replaced by smaller ones after aging. On the other hand, “bee-structures” still appear on the surface of the aged AAD binders, and morphological changes between virgin and aged AAD binder were less obvious compared to the ABD-based binders.

Introduction of the aromatic extract into the aged ABD binder (the third row in Fig. 3) produced dispersed elliptical domains, with “bee-structures” at the center of the domains. This is a similar effect as Pauli et al. observed for the wax-doped binder samples [22]. The aromatic extract is a petroleum-derived rejuvenating agent, and its chemistry supposes to be close to that of the malthene fractions in asphalt binders. Therefore, the mechanism responsible for the formation of the “bee-structures” might occur during the rejuvenation process. The aromatic extract rejuvenated AAD sample exhibited finer-sized “bee-structures” and the amplitude of the undulated “bee-structures” was smaller than that of the virgin and aged ones as indicated by the less noticeable contrast between the ‘bee-structures’ and the matrix. The introduction of the WV oil into the aged binders (both AAD and ABD) did not modify their morphologies significantly, as compared to the aged samples (the fourth row in Fig. 3).

In summary, the addition of the rejuvenators resulted in more significant morphological changes than the aging effect; however, the rejuvenated blends did not always reproduce the microstructures as exhibited on the surfaces of the virgin binders. In addition, the aromatic extract had a stronger impact on the microstructural properties of the binders than the WV oil. The development of asphalt binders’ microstructures depends on the binders’ chemistry and the complicated molecular interactions among the different chemical components and any additives [22]. This helps explain the different surface morphological properties in the binder-rejuvenator combinations examined here.

### Table 5

BBR results at −18 °C for the virgin, aged, and rejuvenated asphalt binders AAD and ABD.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ABD binder</th>
<th>AAD binder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Virgin</td>
<td>Aged</td>
</tr>
<tr>
<td>Creep stiffness (MPa)</td>
<td>760</td>
<td>839</td>
</tr>
<tr>
<td>m-value</td>
<td>0.205</td>
<td>0.159</td>
</tr>
</tbody>
</table>
Histograms of maps (Fig. 4) of the adhesion, dissipation energy and DMT modulus of the virgin, aged and aromatic extract rejuvenated ABD samples are shown in Fig. 5. Bimodal distributions appeared for each mechanical properties of the samples due to the contrast between the dispersed phase (namely the flake-like and elliptical structures) and the matrix. However, the chemical components that are responsible for the different microstructures remain unknown. The flake-like domains observed in virgin and aged ABD samples showed a smaller adhesion, dissipation and DMT modulus as compared to its surroundings, the matrix area. However, the area fractions of the flake-like domains in virgin and aged ABD samples were rather small (the less obvious peaks in the histogram), and therefore only mechanical properties of the matrix are reported as representative values of the sample surfaces. For aromatic extract rejuvenated ABD sample, the bimodal distributions of adhesion and dissipation energy from the dispersed phase and the matrix were more significant. The dispersed elliptical domain possessed a smaller adhesion and dissipation, yet a slightly larger modulus value than the surrounding matrix, which agrees with Fischer’s work [25]. An interesting observation was that for this rejuvenated sample, the modulus contrast between the dispersed domains and the matrix flipped around as compared to the virgin and aged binders, which needs further investigation of the chemical compositions over these different domains.

Aging decreased the adhesion by about 10% (16 nN and 14.5 nN for virgin and aged ABD, respectively). The introduction of the aromatic extract brought the adhesion force on the matrix area back to the level of the virgin binder while the dispersed phase showed a relatively lower adhesion. Upon aging, the dissipation energy also decreased slightly whereas the rejuvenated samples had a similar value of dissipation to that of the virgin binder.

In Fig. 5(c), DMT modulus of the rejuvenated ABD was smaller than both the virgin and aged ones, as could be expected. It is foreseen that aging stiffens asphalt binders (as shown by the DSR measurement); however, the PFT QNM measurements showed that the aged ABD had a slightly smaller modulus as compared to the virgin one, and repetitive measurements did not produce the same trend as captured by DSR tests. This discrepancy might be explained by the fact that PFT QNM and DSR are measuring mechanical properties of asphalt binders at different length scales. It is important to keep in mind that the AFM measurements represent the surface properties of a material that can be different from its bulk properties tested by DSR. How to relate the surface properties at the micro scale with macroscale bulk measurement for different materials is still under careful investigation. In addition, other factors can also influence the accurate measurement of binders’ modulus. For instance, the DMT contact mechanics that is embedded into the PFT QNM mode is proven to be inappropriate for retrieving binders’ modulus according to the calculated lambda value as discussed earlier, similar to the scenario in [26]. For future work, a blunt tip and JKR model are recommended for more accurate microscopic modulus measurements. Another factor affecting accurate
quantitative measurement of the modulus could be the use of the inappropriate tip in terms of the relative stiffness (the ratio of the tip stiffness over the sample stiffness). The Tap150A tips from Bruker are recommended for materials with modulus of 4 MPa–0.5 GPa, which might not be stiff enough for probing binder with higher modulus (i.e., the aged binders).

In general, it was shown that, values of the mechanical properties from microscopic measurements of adhesion and dissipation were consistent with the macroscopic DSR results. For instance, the decrease of the complex viscosity after aging and its recovery upon adding the aromatic extract agree with the changes in the dissipation energy from the PFT QNM measurements. This suggests that aging and adding aromatic extract as a rejuvenator had significant impact on mechanical properties of asphalt binders at both the micro and macro scales. In addition, microscopic mechanical properties’ measurements provide supplementary information for evaluating the rejuvenation effect than merely morphological characterization.

3.3. SARA fractionation

In order to explore how the rejuvenator and different chemical fractions in asphalt binders contribute to their overall mechanical properties and the rejuvenation mechanism, SARA fractionation of aromatic extract alone, as well as virgin, aged and aromatic extract rejuvenated ABD was conducted. As shown in Fig. 6, SARA fractionation suggested that aromatic extract contains ~40% of saturates, ~47% of aromatics, and the rest are resins, with trivial amount of asphaltene fraction, which is different from the manufacturer’s description. To this end, mass fractions of aromatic extract obtained by the authors were used for further data analysis since the SARA fractionation method was used consistently for virgin, aged and rejuvenated samples. For both virgin binders, the resin fraction accounts for the most in their chemical compositions.

Changes in the SARA fractions of the ABD-based samples (Fig. 6(a)) were significant. After aging, the saturate and resin contents did not vary much while the aromatic fraction decreased from 28% to 10%, which led to an overall increase of the asphaltene fraction by about 12%. The effect of aging on ABD is consistent with Qin’s observation [27] that aging converts the aromatics into the asphaltenes whereas it does not have strong influence on saturates and resins. Adding the aromatic extract introduced more saturates and aromatics which, consequently, lowered the fractions of resins and asphaltenes compared to the aged binder. The large amount of saturates contained in the aromatic extract helps explain the significant increase in the saturate fraction in the rejuvenated samples. On the other hand, the rejuvenated sample did not duplicate the mass fractions of the virgin binder.

Similar to the ABD binder, the aged AAD sample had an increase in asphaltenes and a decrease in aromatics, as compared to its virgin binder. The addition of the aromatic extract increased saturates and aromatics content whereas the asphaltene fraction did not decrease much as compared to the aged AAD sample. Also in this case the rejuvenated sample did not duplicate the mass fractions of the SARA components in virgin AAD.

The molecular interactions among the different binder components and additives are very complex. Some chemical components might be converted to others when asphalt binders are subjected to different treatments such as aging and rejuvenation. In this case, one cannot expect that mass fraction of each SARA components in the rejuvenated binders would be equal to the sum of each fraction from the aged sample and the additives based on the proportion of the two used in the blending.

In light of the above analysis and considering the macroscopic and microscopic mechanical properties of asphalt binders ABD and AAD discussed in the previous sections, it is a logical step to conclude that changes in the chemical fractions among the virgin, aged, and rejuvenated binders are responsible for the stiffening effect of aging and the rejuvenating effect resulted from the rejuvenators. This agrees with the suggestion of Roberts et al. [6]
that adding the light bituminous fractions such as aromatics helps restoring the mechanical properties for RAP binders.

4. Conclusions and future work

With the increasing interest in increasing the RAP content to produce more sustainable asphalt pavements, various rejuvenating agents have been added into the mix design so as to restore the rheological and mechanical properties of RAP materials. This is an important step for service-life extension of asphalt concrete pavements made with higher percentages of RAP. In order to better understand the rejuvenating mechanisms, two commonly used rejuvenating agents, WV oil and aromatic extract, were added to two binders from different crude sources. Rheological properties at intermediate and high temperatures were measured using the DSR test, whereas the BBR test was conducted for low temperature measurements. Surface microscopic morphological and mechanical properties were tested using different AFM devices and techniques. Chemical compositions of aromatic extract, virgin, aged, and rejuvenated binders were determined using SARA fractionation. From the above tests, the following conclusions can be drawn:

1. The complete blending of the rejuvenators into the aged binders restored the rheological properties at intermediate and high temperature ranges as well as the low temperature, as measured by both DSR and BBR.

2. The rejuvenating effect depends on both the rejuvenator and the crude source of the binder. On the one hand, for ABB-based binders, 12 wt.% of WV oil reduced the modulus and increased the phase angle by a higher extent than the same dosage of aromatic extract, which may not necessarily be desirable. In this respect the aromatic extract achieved the desired level of rejuvenation on this binder as compared to the WV oil. On the other hand, the rejuvenating effect of aromatic extract for the two different binders was related to the temperature at which their rheological properties were measured.

3. The rejuvenation effect can be characterized at the microscale using AFM. Microscopic morphological and mechanical measurements represent the surface properties of asphalt binders, and they provide complementary information for studying the rejuvenating mechanisms.

4. Aging and rejuvenation led to morphological changes, depending on the specific binder-rejuvenator combination. The rejuvenated blends did not always reproduce the surface microstructures of the virgin binders.

5. Microscopic measurements on adhesion and dissipation of virgin, aged, and aromatic extract rejuvenated ABD samples were qualitatively consistent with the bulk DSR results. However, further investigations are required in order to build the link between microscopic and macroscopic mechanical properties of asphalt binders.

6. Evaluation of the results from the different characterization techniques points out that changes in the chemical fractions of the asphalt binders were responsible for the stiffening effect after aging and the improvement of mechanical properties with the addition of the rejuvenators.

Future work includes modification of the microscopic modulus measurement using AFM and applying the above characterization techniques for various types and quantity of rejuvenators in order to provide insight for optimal design of RAP-based asphalt pavements.

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References


