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Investigating molecular conformation and packing of oxidized asphaltene molecules in presence of paraffin wax

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ABSTRACT

This study investigates the effect of paraffinic wax (as a base component in many commercial rejuvenators) on the rheological and intermolecular properties of aged asphalt binder. Samples of oxidized asphalt binder doped with (1%, 3%, 5%, and 10%) paraffin wax were characterized using the rotational viscometer (RV), dynamic shear rheometer (DSR), bending beam rheometer (BBR) and direct tension test (DTT). The RV results showed an improvement trend in workability of aged binder as wax content increased. The DSR results (for a temperature range of 10–76 °C) showed lower complex modules for wax-doped specimen than control specimen. The BBR test results performed at sub-zero temperature showed that an increase of wax dosage led to higher creep stiffness modulus indicating that the asphalt binder became generally stiffer in presence of wax at low temperature. However, fracture energy measured through DTT test showed a significant reduction in presence of wax. The latter can be attributed to plausible weak secondary bonds between wax and asphaltene molecules as well as crystallization of wax molecules at low temperature within the asphalt matrix. This in turn can lead to wax crystals playing as stress localization point giving rise to crack nucleation at the wax-asphalt interface reducing overall fracture energy; it was further observed that as the wax content increased, the asphalt binder became more brittle.

To further investigate the effect of wax on the molecular conformation and packing in aged asphalt binder, a molecular simulation was performed on a system of wax and oxidized asphaltene. The results of molecular simulations showed a reduction in formation of oxidized asphaltene nano-aggregates as the amount of wax increased in the wax-doped oxidized asphaltene matrix at room temperature, which was also confirmed by size exclusion chromatography. Furthermore, the radial distribution function results showed a less packed structure of oxidized asphaltene molecules in presence of wax molecules. Increasing the wax content also increased the diffusion coefficient of wax into the oxidized asphaltene matrix within a solvent medium. It was also showed that interaction energy of a dimer of oxidized asphaltene is at a lower energy state in presence of wax molecules, which suggests that wax molecules can promote dimerization of oxidized asphaltene molecules while suppressing nano-aggregates formation.

1. Introduction

Known as a good adhesive in the construction sector, asphalt binder has been used in more than 90 percent of paved roads in the U.S. [27,46]. The asphalt binder used in hot mix asphalt is always susceptible to reaction with oxygen in the air, a process called oxidative aging [34,52].

Oxidative aging is a major factor responsible for hardening and rheological changes in asphalt, resulting in degradation of desirable asphalt properties [8,13,44,47]. The oxidative aging process happens in two stages; for each stage, there is a laboratory test method to simulate it. The rolling thin-film oven (RTFO) test is used to simulate short-term aging that happens during the construction phase; the pressured aging vessel (PAV) test is used to simulate long-term aging of asphalt binder [11,19,36,40,49]. The use of reclaimed asphalt pavement (RAP) has been highly promoted by both road authorities and asphalt contractors; mainly due to increase and fluctuation of asphalt binder price from \$235 per ton in 2006 to \$635 in 2015 and to \$409 in 2018 based on asphalt price index [28]. Another motivation for promoting use of RAP is its abundance in the US., as well as the potential environmental

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benefit from reduction of use of natural resources and virgin bitumen which can off-set some of the consumption of depleting resources of virgin binder and mineral aggregate [30].

To allow usage of high RAP asphalt mixture, a rejuvenator is needed to retrieve the original mechanical properties of virgin asphalt binder. Currently, different types of rejuvenator for aged asphalt have been introduced to the market; these rejuvenators have different origins such as bio-based (wood pellets, animal waste, soybean and corn stover), waste engine oil, and some refinery-based oils that have portions of paraffinic oil bases [53,9,29]. N-alkane is a saturated hydrocarbon (C_nH_{2n+2}) (also called wax) that can be in form of a gas for n less than 5, a liquid for n between 5 and 17, and a solid for n greater than 17 [16]. Many newly used rejuvenators contain paraffinic wax or paraffinic oil [25]; these still have the viscosity-lowering effect, but there is still the question of their effectiveness in chemically rejuvenating aged asphalt. Previous researches studied rejuvenators which contained paraffinic oil base. Mogawer et al. [25] used paraffinic oil as rejuvenator and showed that it improved cracking properties of asphalt mixtures containing 50% RAP binder. For instance fatigue test shows a much higher number of cycles (two times of control binder) to failure point. Zaumanis et al. [53] introduced waste engine oil with paraffin wax to mixtures made from 100% RAP binder; the latter showed improvement in creep compliance which was increased by 25% compared to reference binder. Wang et al. [50] used a warm mix additive with structure of a polyethylene wax as rejuvenator for high RAP mixtures and showed improvement of high and low temperature properties.

Among the four different chemical groups known as SARA (saturates, aromatics, resins and asphaltenes) [14], asphaltenes are the highly polar constituents of asphalt binder that are dispersed in the maltene phase [1]. A change in the concentration of asphaltenes in asphalt binder causes a variety of changes in the asphalt's rheology as well as the asphalt's mechanical properties [18]. The asphaltene molecules and their self-interaction are recognized to strongly affect the rheological and mechanical behavior of asphalt binder [22,26]. During the aging process of asphalt binder, one of the major factors that contributes to the stiffening of asphalt binder is the oxidation of polar aromatics, and asphatenes, leading to an increased aggregation due in polar fraction of asphalt components [42]. It has been documented that oxidation increases the asphaltene fraction of binder as the aromatics convert to asphaltenes [35]. The results of gel permeation chromatography (GPC) indicated an increase in high molecular size species after asphalt was exposed to oxidation; the latter was attributed to asphaltene molecules becoming more prone to aggregation due to oxidation [39].

Other studies focused on examining interactions of wax with other constituents of asphalt binder in micro scale [12,15,33,38]. The effects of paraffin wax on unaged asphalt binder at both macro scale and nano scale was also studied by [37]. However, the effect of paraffin wax materials on aged asphalt binder and understanding the connection between molecular interactions and rheological properties of aged asphalt is yet to be investigated.

Furthermore, there are limited study of the effect of wax on asphaltene behavior (as one of the key players of asphalt properties), especially after oxidation of asphaltene during aging process, and its effect on asphaltene nano-aggregates formation.

This paper examines molecular conformation and packing of oxidized asphaltene molecules in presence of paraffin wax via both computational modeling and experiments. Accordingly, the paper presents a comprehensive thermos-mechanical characterization aged asphalt binder doped with different dosages of paraffin wax utilizing a rotational viscometer, a dynamic shear rheometer, a bending beam rheometer, and a direct tension test. The Size exclusion chromatography was done to study the effect of paraffin wax on the formation of nanoparticles. To further study the intermolecular interactions between paraffin wax and aged asphaltene molecules, an equilibrium molecular dynamics simulation has been performed using Large-scale Atomic and Molecular Parallel software in the MedeA® 2.2 environment. The simulations took place on a simplified model of the wax and oxidized asphaltene complex in two stage: first, the effect of doped n-Paraffin wax on the self-association of oxidized asphaltene molecules was studies; second the behavior of wax molecules in a complex of asphaltene-wax in methanol as a solvent medium was studied. The result of this study provides in-depth understanding on how paraffin wax affects molecular packing of oxidized asphalt binder, and consequently its thermo-mechanical properties.

2. Experiment details

2.1. Experiment plan

The asphalt binder used in this study was graded as PG 64–22 and donated by Associated Asphalt Inc. of Greensboro NC; it was aged based on RTFO (short term aging simulator) and PAV (long term aging simulator) based on the standards [2,5] and doped with different paraffin wax dosages. For the aging process, the binder was initially aged using a rolling thin-film oven followed by two durations of the regular aging procedure of a pressure aging vessel. The test using two durations is known as 2XPAV, total of 40 h. 2XPAV has been shown to give better results with regard to the long-term aging that happens in the field [8]. The wax that was used for aged asphalt binder modification was a petroleum based paraffin wax (P31, with melting point of 53–57 °C, purchased from Fischer Scientific). The wax was blended at 1%, 3%, 5%, and 10 %wt of the initial aged asphalt binder, and samples were hand-blended at 135 °C for 30 min.

The viscosity results were determined using a rotational viscometer (RV). Measurements were conducted following ASTM D4402 [3] using a Brookfield Viscometer RV-DVIII Ultra, by applying a rotational shear on the selected material. Samples were prepared by pouring 10.5 g of each sample (aged binder with different concentrations) into an aluminum chamber following by cooling to room temperature. Samples were preheated in an oven for 30 min before testing in the temperature-controlled thermoset apparatus. After reaching thermal equilibrium, three viscosity results were taken at three-minute intervals until the results had a range of less than 100 cP (0.1 Pa·s). The average value of three readings was taken as the viscosity value. The speed chosen for this study was 20 rpm performed at 120, 135, and 150 °C.

The complex moduli results were determined using the Malvern Kinexus Pro dynamic shear rheometer (DSR) following ASTM D7552 – 09 [7]. Each sample (three replicates for each sample was tested) was test at 31 different frequencies ranging from 0.1 to 100 rad/s at a temperature range of 76–10 °C with 6-degree increments. The 25 mm spindle was used for the high intermediate temperature range of 64–76 °C, while the 8 mm spindle was used for 58–10 °C due to increased stiffness of the binder at lower temperatures [20]. From the resulting data, master curves were generated using the principle of time–temperature superposition (TTS) using the Williams-Landel-Ferry method (WLF) [51] at a reference temperature of 43 °C. Furthermore, the temperature at which the loss moduli and storage moduli meet (known as the crossover temperature) was measured as a property of the material. In general, viscoelastic materials with higher crossover temperature reach their elastic behavior faster as temperature drops and behave more as a stiffer material [17,37].

The bending beam rheometer (BBR) was used to evaluate the modified aged binder's stiffness and ability to relax (m-value) at low temperature and compare it to that of unmodified aged binder. For the low-temperature testing, −12 °C was selected, following the SuperPave binder PG specification, which requires the binder to be tested at the low-temperature grade of the binder (PG 64-22) plus 10 °C, as mentioned in ASTM D6648 [6]. Asphalt binder sample beams were prepared by pouring the binder into aluminum molds (four replicates). The samples were allowed one hour to cool to room temperature, then placed in a freezer for five minutes before being demolded. A constant