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Full Length Article

Characterization of oxidized asphaltenes and the restorative effect of a bio-modifier

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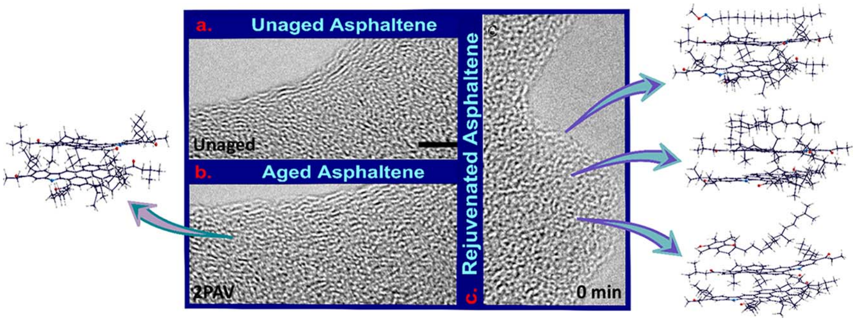
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we use density functional theory (DFT) at a micro-level and laboratory experiments at a macro-level to understand two phenomena: the molecular mechanisms responsible for the chemical aging of asphalt, and the restorative effect of a new generation of bio-modifiers for treating aged asphalt. Our DFT-based studies show that the interplay of a series of competing factors is responsible for enhancement of the intermolecular interactions in aged (oxidized) asphaltene dimers compared to unaged (unoxidized) forms. While electron-withdrawing groups of carbonyl (C═O) around the aromatic core decrease the spatial extent of the π-electron cloud and unfavorable repulsion interaction, they reduce the electron density and subsequently reduce some favorable non-covalent interactions in this region. The loss of electrostatic quadrupole-quadrupole interactions in the aromatic center is partially compensated for by new forms of electrostatic interactions in another part of the molecule. Next, we use a modifier derived from animal waste to rejuvenate the oxidized asphaltenes. DFT results show that the main components of the bio-rejuvenator are able to mitigate the effect of polar substitutions generated through oxidation. Interestingly, the chemical nature of asphaltenes in our bio-rejuvenator is dramatically different from asphaltenes of aged or unaged asphalt. The FTIR picture of the bio-rejuvenator asphaltenes shows the aromatic cores with shorter aliphatic side chains and many more ether and hydroxyl side groups. HRTEM images confirm the disturbance of the aged asphaltene agglomerates and enchantment the lattice spacing in the presence of the target bio-rejuvenator.

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1. Introduction

“Asphalt” is a mixture of minerals bound together with a kind of adhesive material called “asphalt binder” or “bitumen”. Asphalt binder is a highly viscous and waterproof material with excellent adhesive properties that is produced through vacuum distillation of crude oil and used as the black glue to amalgamate mineral fillers in the top layer of asphalt pavements. Throughout the present text, our usage of the words “asphalt” or “binder” refer to “asphalt binder”.

Asphalt binder is an end product of a natural organic source, so it is susceptible to oxidative aging when exposed to atmospheric oxygen. Oxidation is one of the critical factors contributing to the hardening of asphalt and the consequent pavement embrittlement that eventually leads to deterioration of asphalt’s mechanical properties and performance [1,2]. The major consequence of the irreversible oxidation process is an increase in the viscosity of asphalt that is mainly attributed to two factors: a) the evaporation of light asphalt components and the reduction of the maltene/asphaltene phase ratio (maltene is the liquid phase, and asphaltene is the solid phase of asphalt); and b) the oxidation of highly reactive hydrocarbons and polar species that leads to a change in functional group composition and increased concentration of asphalt’s polar components [3]. Asphalt hardening due to the evaporation of volatile components is not comparable to what takes place when the asphalt composition changes due to the oxidizing process[4]. The latter factor is the main focus of this paper.

During oxidation, the introduction of polar functionalities on asphalt fractions is believed to cause further molecular agglomeration due to increased polar association forces such as hydrogen bonding, van der Waals forces, and Coulombic interactions; an additional factor is the aromatization of reactive compounds such as polycyclic hydrocarbons, which makes them more planar and consequently more susceptible to agglomeration. Thus, increases in asphaltene agglomerates and asphaltene content are significant characteristics of an oxidized binder [5]. Indeed, it is generally accepted that aromatic and resin components are converted to asphaltenes during oxidative aging. making aged binder rich in asphaltenes [6,7].

One of the most appealing counteractions to the aging of asphalt binders is applying “rejuvenators”. A rejuvenator should be composed of fragments that re-establish the chemical compatibility of asphalt binder and mitigate the aggregation of components after aging. It should be noted that the terms “rejuvenator” and “additive” (softening agent) are mostly referring to two distinct functions [8]. The rejuvenation treatment of “additives” is typically limited to a softening effect (lowering the viscosity) due to the addition of small molecules to the stiff and brittle aged asphalt. Additives may not restore the original level of peptizing found in unaged asphalt. True rejuvenators, on the other hand, are aimed at restoring the physical and chemical properties of oxidized binder by rebalancing the colloidal structure as well as restoring the aged asphalt's original viscosity [9,10].

In recent years, research has focused on a new generation of asphalt modifiers derived from biomass as promising candidates for rejuvenating agents. The primary source (biomass) of bio-rejuvenators encompasses a range of biodegradable substances with animal or vegetal origin, such as wood-based materials [11,12], microalgae [13], waste cooking oil [14], corn stover [15], and swine waste [16–18]. These bio-additives present different functions from partial replacement as modifier to direct alternative for asphalt binder [15].

Through a comprehensive study conducted by our research team, we have shown that the bio-oil derived from swine manure is a potential alternative for petroleum-based asphalt binders [16,18]. We have also shown that asphalt binder modified by the bio-residue derived from swine manure is less susceptible to oxidizing agents [19]. In our comparative study of wood pellet, corn stover, miscanthus, and swine manure, we found that vegetal-based bio-oil, due to its carbohydrate nature, has a higher percentage of oxygen-containing compounds that make them relatively proper targets for oxidizing agents compared to swine-manure-based bio-oil with its high content of nitrogen compounds [20]. Moreover, the vegetal-based rejuvenators showed a higher fraction of compounds not soluble in n-heptane compared to rejuvenators based on animal waste.

The present study starts by characterizing the intermolecular interactions between asphaltene planes before and after aging. This evaluation is based on quantum studies at the density functional theory (DFT) level, and our focus is on refining energy parameters, d-spacing, and electronic analysis of the agglomerates before and after aging. The principal components of this bio-modifier from swine manure have been chemically characterized with GC–MS (gas chromatography–mass spectrometry) and NMR [16], so we can continue the DFT analysis by studying the alteration of the behavior of an oxidized asphaltene dimer in the presence of the isolated individual principal molecules of bio-modifier, to establish a correlation between the chemical nature of the bio-modifier components and the extent of their rejuvenation effect on the oxidized asphaltene. Based on our micro-level understanding of the system, we try to explain our laboratory findings and observations at a macro scale. So, in the next step, high resolution transmission electron microscopy (HRTEM) is used to examine the molecular packing of unaged, laboratory-aged, and bio-modified aged asphaltene samples. Fourier transform infrared (FTIR) spectroscopy is also used to provide additional information on the physical and chemical nature of these compounds.

2. Materials and Experimental Methods

2.1. Sample preparation

The neat asphalt binder grade selected for this study was Superpave PG 64-22, a binder grade commonly used in the U.S. It was acquired through Sharpe Brothers in Greensboro, NC. The bio-oil rejuvenator was derived from swine manure as described elsewhere [16].

Virgin asphalt binder was aged in the laboratory for comparison. Laboratory aging was performed following the aging method documented by Bowers et al. [21]. This method involves the sequence of a rolling thin-film oven (RTFO) followed by double the standard duration in a Pressure Aging Vessel (2PAV). RTFO aging was performed following ASTM D2872, in which samples were aged in an RTFO at 163 °C for 85 min while being subjected to an airflow of 4 L/min. This aging procedure simulates asphalt binder that has undergone aging while being mixed with aggregate at an asphalt-mixing plant and then placed in the field. The sample was then exposed to double the standard duration of PAV aging, according to ASTM D6521. Approximately 50 grams of asphalt binder were placed onto plates and subjected to 2.10 MPa air pressure at 100 °C for 40 h. Samples were then degassed using the vacuum oven at 170 °C for 30 min at 15 kPa to remove air bubbles entrapped by the PAV aging. As shorthand in this manuscript, the laboratory-aged binder is referred to as “2PAV”. To prepare rejuvenated samples, 2PAV-aged binder was hand-blended with dosages of rejuvenator ranging from 5 to 30% for 5 min at 135 °C.

2.2. HRTEM and ATR-FTIR measurements

High resolution transmission electron microscopy (HRTEM) on asphaltene fractions was performed using a JEOL 2010 Advanced High Performance TEM operating at 200 kV. Samples were prepared by first dissolving the asphaltenes in toluene at roughly 5 mg/mL and quickly adding about 10 times volume of methanol in an attempt to flocculate the solution and produce small agglomerates. The unaged asphaltenes did not flocculate until a trace amount of water was added. Then, 200 mesh copper grids with lacey Formvar/carbon support were dipped into the suspensions and allowed to air dry. Atomic fringe spacings were measured using Gwyddion image analysis software by selecting areas of the imaged asphaltene surfaces and finding the peak frequency in the radial power spectral density function (PSDF).