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Changes in fractional compositions of PPA and SBS modified asphalt binders

Shahriar Alam[a], Zahid Hossain[b,*]

[a] *Arkansas State University, Jonesboro, AR 72467, USA*
[b] *Arkansas State University, PO Box 1740, Jonesboro, AR 72467, USA*

HIGHLIGHTS

- The crude origin defines the response to any modification.
- Asphaltenes increase linearly with PPA modification.
- Viscosity values increase linearly with Asphaltenes percentage.
- PPA modification has an optimum dosage level.
- SBS modification rearranges the fractions rather changing their percent quantities.

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ABSTRACT

Asphalt binders are complex chemical composites of various organic molecules. They are often modified chemically to obtain some rheological and physical superiority over the unmodified neat binders. The chemical compositions they inherit from their crude origins determine the suitable modification methodologies, which eventually lead to their rheological changes. The changes in chemical compositions due to the modifications of selected asphalt binders with Polyphosphoric Acid (PPA) and Styrene Butadiene Styrene (SBS) were observed in this study. The percentage fractions of Saturates, Aromatics, Resins, and Asphaltenes (SARA) were measured for binders modified with different amounts of PPA and SBS. The Asphaltenes content was found to increase linearly with the addition of PPA and SBS, and so did their viscosity values. Unlike acidic binders (pH < 7.0), basic binders (pH > 7.0) demonstrated a distinctive decline of pH with PPA modifications. The Aromatics and Resins contents had a sharp change after a certain amount of PPA that demonstrated a demarcation point beyond which further addition of PPA would result in no desirable benefits. The demarcation points were different for two different (crude origin) binders. The addition of SBS did not contribute in changing the Asphaltenes content. Rather, SBS changed the Aromatics and Resins contents to yield the desired paving grade binder.

1. Introduction

Asphalt binder is the remainder fraction obtained as a heavy semisolid or residue of crude oil distillation processes. Crude oils being originated from different sources inherit different chemical compositions, and so do their remainder fractions. An asphalt binder is a complex mixture of hydrocarbons, typically in the range of 24–50 carbons [1]. The elemental compositions of different asphalt binders are primarily dependent on their crude origins. Any generic composition is quite tough to formulate on the basis of geographical domain [2]. Even the density of asphalt binder is described at a range that lies between 1.01 and 1.04 g/cm^3, which is also a source specific property [3]. It is conceivable that an asphalt binder with a higher density can also be termed as a harder binder. As a consequence, the so-called binder stiffness also varies at a wide range.

Asphalt binders for paving construction are typically modified with blown air before they are being modified by using additives [4]. Other than the blowing operation, asphalt binders are often modified chemically to attain certain rheological superiorities over the neat unmodified binders. Polyphosphoric Acid (PPA) and Styrene Butadiene Styrene (SBS) have long been used in asphalt modifications by refineries. However, some state departments of transportation (DOTs) have bans on PPA alleging it to be the cause

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* Corresponding author.
E-mail addresses: mdshahri.alam@smail.astate.edu (S. Alam), mhossain@astate.edu (Z. Hossain).

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of some premature pavement distresses such as striping. PPA and SBS have some beneficial implications too. This study aims at identifying the changes in chemical compositions of unmodified and modified asphalt binders collected from two local sources (refineries).

1.1. Literature review

The chemical complexity of an asphalt binder precludes any precise molecular identification [5]. This formulates the approach of analyzing asphalt binders based on families of compounds. These families are termed as Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (As), which are often called as *the SARA fractions*. The molecular weights of SARAs vary between 300 and 1000 Daltons [6]. As stated by Lesueur [7], "Bitumen must be thought of as a chemical continuum with gradual increase of molar mass, aromatic content and polarity from saturates to asphaltenes." The SARA fractions keep on forming larger molecules through associations. Saturates are wax-like simple aliphatic chain compounds. This waxy component constitutes a little portion of the bulk asphalt binder. Saturates have a very low glass transition temperature around −70 °C, which keeps it at a liquid state at a room temperature [8]. Saturates contain a few crystalline linear n-alkanes with a very few polar atoms or Aromatics ring [7]. The ratio of number of Hydrogen to Carbon atoms (H/C ratio) of asphalt binders generally lies at around 1.5, which indicates a presence of many heteroatoms along with the abundance of hydrocarbons. The maximum possible H/C ratio is four (4) for CH_4, and it gradually approaches to two (2) as the hydrocarbon chain grows longer. The Aromatic compounds present in asphalt binders contain many heteroatoms that makes the H/C ratio smaller than 2. The typical H/C ratio of Saturates is close to two (2) with only traces of hetero atoms [7]. The Aromatics are cyclic compounds with some heteroatoms. They are also termed as naphthene Aromatics. The Aromatics fraction chiefly makes up the continuous phase of the so-called asphalt colloidal model. They further associate and form Resins that contain some heteroatoms such as nitrogen and sulphur. Saturates and Aromatics are oily liquids at room temperature, whereas the Resins are solid [8]. The compositions of Resins are very close to that of Asphaltenes except their lower molecular mass [9]. The Asphaltenes are the solid phase present in the asphalt colloidal model. It is the most polar fraction with many hetero-atoms. Asphaltenes are the mostly studied for its viscosity building role. The average molecular structures of Asphaltenes have been proposed by some researchers, which states that Asphaltenes contain more condensed aromatic rings and more polar groups [10]. The presence of fused aromatic structures seems to be the fundamental feature that makes Asphaltenes different from the remaining parts of the asphalt binder [7]. Asphaltenes form almost planar molecules that associate through π-π bonding forming a stacked structure like graphite [11].

The SARA fractions increase the aromaticity and heteroatomic contents in the order S < A < R < As [12]. The Aromatics and saturates serve as the continuous phase while the Asphaltenes remain as the dispersed phase stabilized by the Resins in the continuous matrix. The dispersion was addressed by a colloidal bitumen model proposed by Pfeiffer [13]. According to the colloidal model, the Asphaltenes are the solid phase remaining dispersed in the maltenes. The Asphaltenes are somewhat spherical [14], cylindrical [15], or flat sheet [16] objects stabilized by a peripheral Resins layer [7]. Asphaltenes aggregate and Resins remain dispersed in the continuous medium of Aromatics and Resins. PPA strongly interacts with the Asphaltenes fraction leaving the Maltenes fraction unaffected [17]. Although the reaction mechanism has still not been understood entirely because of its compositional diversity, the mechanism has been proposed by some researchers. According to Fee et al. [18], PPA donates an H^+, which could be an initiator of interaction with asphalt binders.

Asphalt binders are often modified by PPA to improve their performance. The performance grade (PG) system requires expanding the useful temperature interval (UTI) for binders those are required to be used in high pavement temperature regions. According to a recent study [19], achieving the UTI greater than 92 °C requires some sort of modification to the neat (unmodified) binder. The PPA is an oligomer of H_3PO_4, which is obtained through dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4 [20]. A number of possible reactions between PPA and asphalts obviously exist where no single reaction is satisfactory by itself [19]. The reaction is primarily dependent on the base asphalt. PPA reacts with the asphalt binder through phosphorylation [17]. However, PPA helps elevate the higher temperature grade, and thus the rheological properties without affecting the low temperature properties [19]. The addition of PPA serves increasing the viscosity without negatively affecting the penetration values. In contrast to air blowing operation, PPA has gained the popularity due to its capability of modifying asphalts in an easily controllable way. Typically 1% of PPA helps elevate the PG by one full grade [17]. It was stated that PPA acts through neutralization of polar interactions between the Asphaltenes molecules, either by protonation or esterification [17]. Eventually the effect is an increase in solvation of the Asphaltenes, which in turn increases the viscosity [17]. According to Baumgardner [19], the co-polymerization of the Saturates, cross linking the neighboring asphalt segments, the cyclization of alkyl Aromatics occur due to PPA addition.

On the other hand, elastomers such as SBS are frequently used in asphalt modification. It increases the kinematic and dynamic viscosity values of asphalt binders [21]. SBS being a polymer can perform far better in combination with PPA than SBS or PPA alone [17]. Typically, every 1% of added SBS helps elevate 3 °C in high temperature grade. Four different asphalts with both SBS alone and SBS & PPA combined were taken into consideration to observe the changes in chemical composition due to SBS addition.

1.2. Objectives

The primary objective of this research was to examine the changes in the chemical compositions of PPA- and SBS-modified asphalt binders. Since an acid (PPA) was used as a modifier, the pH values were evaluated for all the binders to observe the degree of modification. The SARA fractions were considered to quantify the compositional changes. Effects of these fractions on some of the rheological properties of the tested asphalt binders were discussed. Acid numbers of the tested asphalt binders were also determined. Any distinguishable pattern in compositional changes was aimed to be delineated.

2. Materials and methodologies

The variation of chemical compositions of asphalt binders is entirely source specific. The test samples were collected from two different crude sources, namely, Source-1 (S1) and Source-2 (S2). These binders were modified with different percentages of PPA and SBS to raise their higher PG grades. Details of tested samples are presented in Table 1. Two PG 64-22 binders (S1B1 and S2B1) from two different sources were modified with different amounts of PPA, SBS, or a combination of both PPA and SBS. For each of the neat binders (S1B1 and S2B1), PPA was added 0.25% higher (Samples S1B2 and S2B2) and 0.25% lower (Samples S1B4 and S2B4) than the optimum PPA dosage (0.5% for S1B1 and 0.75% for S2B1) needed to raise their grade to a PG 70-22 (S1B3 and S2B3). PPA is available in various grades. The PPA used in this study was of 105% grade. The SBS used in this study was commercially available as Vector Dexco 2411. A high-level outline of the workflow has been illustrated in Fig. 1.

A majority of the modifications of these binders were done in a commercial laboratory. The optimum dosages of PPA were selected based on selected chemical properties of the corresponding crude oils and their distillation residues, and pro-