Implications of physico–chemical interactions in asphalt mastics on asphalt microstructure

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HIGHLIGHTS

- Asphalt mastics are evaluated using Atomic Force Microscopy.
- Physico–chemical interactions in mastics alter asphalt morphology.
- Filler specific surface area affects extent of physico–chemical interaction.
- Physico–chemical interactions alter asphalt mastic rheology.

ARTICLE INFO

ABSTRACT

Asphalt binder and filler blend to form asphalt mastic, which constitutes the effective adhesive film in asphalt concrete. Pavement performance can be improved through better engineering of the mastic, which requires a fundamental understanding of the interaction between asphalt and filler. Physico–chemical interactions result in adsorption of polar fractions of the asphalt onto filler surfaces, leading to the formation of an interphase layer on the surface of particles and modifying the asphalt binder matrix. This study seeks to investigate the effects of physico–chemical interaction on binder matrix microstructure using Atomic Force Microscopy (AFM) and qualitatively relate microstructural findings to macroscopic rheology.

1. Introduction

Asphalt concrete is a composite material consisting of aggregates of varying size, asphalt binder, and air voids. Coarse aggregates in asphalt mixtures are effectively coated by a blend of asphalt binder and filler, termed asphalt mastic [1]. Fillers consist of particulate matter less than 0.075 mm in diameter [2]. Fillers used in asphalt concrete include both natural and manufactured origins [3]. Natural fillers are the dust portion of mineral aggregate. Manufactured fillers, on the other hand, are produced as by-products of industrial processes (e.g., fly ash). The mastic constitutes the weakest phase of asphalt concrete and therefore performance of asphalt pavements is highly correlated to the properties of the mastic. It has been demonstrated that filler can significantly influence constructability, oxidative aging, stiffness,

fracture resistance, and moisture susceptibility of asphalt concrete [3]. Current Superpave asphalt concrete specifications include provisions for filler only through specifying an allowable range of mass ratios between filler and effective binder [2]. These specifications were developed based on empirical observations. While a great deal of research has been conducted to understand the performance of binders and mixtures, relatively little attention has been given to the asphalt mastic and correspondingly, filler. An improved understanding of the interaction between filler and asphalt binder could lead to improved engineering and specifications of fillers in asphalt concrete and hence, improved performance of pavements.

Various studies have shown there are three primary mechanisms by which fillers reinforce asphalt binder [4–6]: volume filling, particle structuralization, and physico–chemical interactions. Volume filling and particle structuralization are both means of mechanical reinforcement. Volume filling increases asphalt mastic stiffness simply as a result of the replacement of asphalt binder volume with rigid particles. Filler particles start to form an interconnected network at a filler volumetric concentration of roughly

40%, leading to a rapid increase in the rate of stiffening with increasing volume fraction [6–8]. At lower filler concentrations, particle contact is not established and the mastic will behave as a dilute suspension, with volume filling constituting the dominant mechanical reinforcement mechanism. The third type of reinforcement, physico–chemical interaction, involves the adsorption of polar fractions of the asphalt binder onto the surface of filler particles [5,9,10]. Physico–chemical interaction is illustrated in Fig. 1. Physico–chemical interaction leads to formation of an interphase adsorbed layer of the polar fractions of asphalt on the surface of filler particles. In addition, loss of certain components of the asphalt to adsorption modifies the chemistry and morphology of the non-adsorbed, "effective" binder matrix.

While mechanical reinforcement mechanisms can be readily inferred from observed mechanical behavior, understanding physico–chemical interactions is more challenging using macroscopic measures. Several researchers have inferred physico–chemical interactive effects through rheological measurements coupled with micromechanical models assumed to accurately reflect macroscopic mastic behavior with emphasis on the thickness and effective properties of the adsorbed layer [11,12]. Others have inferred physico–chemical effects through thermodynamic measures. Craus et al. [10] investigated physico–chemical interactive effects through measuring heat release using a differential microcalorimeter. In addition, researchers have investigated changes in glass transition temperatures between binder and mastics of varying concentrations to investigate physico–chemical interaction effects on matrix properties [5] and adsorbed interphase layer thickness [13]. The majority of past research efforts have focused on identifying interphase layer effects with little consideration to the modified asphalt matrix characteristics. Understanding the physico–chemical interaction between asphalt and filler on the resultant asphalt matrix is critical to enable improved design of mastics.

Asphalt is comprised of a complex, heterogeneous blend of aliphatic and aromatic hydrocarbons with moderate amounts of sulfur and trace amounts of oxygen, nitrogen, and other elements including metals [14]. This complex chemistry gives rise to composite structure in asphalt binders on the order of nanometers to micrometers. Hence, understanding the effects of physico–chemical interaction between asphalt binder and filler on the effective asphalt matrix properties is critical to improved engineering of mastics. Recently, there has been significant advancement in understanding asphalt binder microstructure through use of Atomic Force Microscopy (AFM) [15–18]. AFM is a type of scanning probe microscopy in which a very fine cantilever tip is rastered across the surface of a specimen to map the distribution and properties of constituent phases. The opacity of asphalt does not lend well to optical microscopy methods, making scanning probe microscopy an attractive method for studying binder microstructure. Non-contact or tapping mode, where very small forces are applied as the cantilever is rastered across a specimen's surface, has proven useful in studying soft materials, like asphalt, for obtaining images of surface topography and phase contrast which can be used to identify different microstructural phases in a material. In addition, spectroscopy mode, in which the cantilever tip moves vertically into a specimen rather than across its surface, can be used to perform nanoindentation experiments for measurement of stiffness and adhesive characteristics. Recent research has shown that asphalt binders consist of a variety of microdomains [16,17] with varying rheological properties [18].

Limited research has also been conducted to understand the effect of filler on binder morphology using AFM. Tan and Guo [19] used AFM to study the interaction between asphalt and filler by preparing asphalt droplets which were placed in contact with slices of aggregate. The relative roughness of different aggregate

surfaces along with interfacial region with asphalt was measured using AFM. It was demonstrated that a 2–5 μm gap existed between asphalt film and filler which the authors attributed to surface tension between the filler and asphalt. In addition, nanoscale adhesion tests were conducted which demonstrated an increase in adhesion with addition of filler up to filler volumetric concentrations ranging from 0.1 to 0.2 at which point subsequent addition of filler resulted in a decrease in adhesion. However, no AFM experiments were conducted directly on asphalt mastics. Nazzal et al. [20] studied the dispersion of nanoclay modifiers in asphalt binder using AFM, which the authors concluded indicated the nanoclay was well dispersed within the asphalt. Despite no observed differences in morphology, the inclusion of the nanoclay significantly altered the adhesive forces of asphalt materials based on nanoindentation experiments. Nanoclay dosages studied were 2% and 4% by weight of binder, which is substantially lower than typical filler concentrations in asphalt mastics. Also, nanoclay particles are much finer than typical mineral fillers and thus, further study of morphology implications of fillers on asphalt binders is needed.

This study seeks to investigate the effects of physico–chemical interaction between asphalt and filler on "effective" binder matrix microstructure using AFM and qualitatively relate microstructural findings to macroscopic rheology.

2. Materials and methods

2.1. Materials

An unmodified binder with a PG grade of 64–22 was used in this study. The binder was mixed with three different fillers: granite, Portland cement (PC), and hydrated lime to produce mastics. The granite is a natural filler whereas PC and hydrated lime are both manufactured fillers. The specific gravity and specific surface area (SSA) of each filler are presented in Table 1. Specific surface area was measured using a Quantachrome Monosorb single-point BET surface area analyzer. The Brunauer–Emmett–Teller (BET) theory was used as the analysis technique for SSA measurements. Specific surface area is an important factor governing physico–chemical interaction intensity as greater specific surface areas indicate greater opportunity for adsorption [5]. Each filler was blended with binder at a volumetric concentration of approximately 24%, leading to dust to binder mass ratios ranging from 0.8 to 1.0, within the specified range in Superpave mix design specifications [2]. Use of higher concentrations was avoided to minimize reinforcement by particle-to-particle contact which becomes most prevalent at volume concentrations greater than 40% [6,7].

All of the mastics in this study were mixed with a laboratory stand mixer with supplemental hand mixing to initially agitate mastics. Before mixing, the binder and filler were heated at 150 °C for 30 min and then poured into pre-weighed pint-sized containers. The binder was then transferred to a hot plate to keep the binder fluid during mixing. The oven-heated filler was slowly poured into the binder while agitating. The mastic containers were then covered to avoid dust contamination and allowed to cool at room temperature. In order to prevent variations in thermal history the binder sample source was also placed in the oven at 150 °C for 30 min prior to creating test specimens.

2.2. Experimental methods

Each mastic as well as the bulk binder was tested using the Dynamic Shear Rheometer (DSR) to determine rheological properties. In addition, AFM in Tapping Mode to investigate microstructural implications of physico–chemical interactions between filler and binder on the effective binder matrix.

2.2.1. Dynamic Shear Rheometer

Rheological properties of each binder and mastic sample were determined using an ARG-2 Dynamic Shear Rheometer (DSR) from TA Instruments. Frequency sweep tests at multiple temperatures were used to generate the dynamic shear modulus master curve for all binders and mastics. The frequency sweep test applies cyclic strain at constant amplitude over a range of loading frequencies and temperatures. Loading was applied at frequencies ranging from 0.15 Hz to 25 Hz. The frequency sweeps in this experiment were run at 64, 50, 35, 20, and 5 °C. The 8 mm parallel plate DSR geometry was used for test temperatures of 5, 20, and 35 °C whereas the 25 mm parallel plate geometry was utilized for testing at 50 and 64 °C. Time–temperature superposition was utilized to construct dynamic shear modulus master curves.