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Nanoindentation investigation of asphalt binder and mastic cohesion

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HIGHLIGHTS

- A new approach to obtain cohesive properties using nanoindentation is presented.
- Work of effective cohesion is determined for three asphalt binders and 30 mastics.
- Evidence of a critical filler volume fraction for effective cohesion in mastic.
- Consider volume-filling, particle interactions, and physicochemical interactions.

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ABSTRACT

A nanoindentation technique for determining the cohesive properties of neat, modified, and aged asphalt binders and mastics with varying filler volumetric concentrations is developed, tested, and verified. Cohesive properties of binder and mastic are critically important to the fracture resistance of asphalt concrete. A new approach to calculate and interpret important cohesive properties from nanoindentation data through low-load sphero-conical (blunt) nanoindentation is presented. Work of effective cohesion values are determined as the average response over multiple possible microstructures for three asphalt binders and 30 different mastics of varying filler volumetric concentrations. Results point to evidence of a critical filler volume fraction beyond which further addition of filler does not affect work of effective cohesion. This plateau in work of effective cohesion values is speculated to be related to the combined effects of volume-filling, particle interactions, and physicochemical interactions. The critical filler volumetric concentrations corresponding to the plateau in work of effective cohesion range between 0.20 and 0.30, which is within the range from literature of 0.15–0.30. Testing of binder and mastic through nanoindentation is an important step toward in situ testing of mastic within asphalt concrete, which is inaccessible using conventional macroscopic experimental methods.

1. Introduction

A need currently exists to develop an accepted measurement technique for characterizing the cohesive properties of asphalt binder and mastic that can motivate and enable multiscale and macroscale modeling approaches. Cohesion is important in asphalt performance as an indicator of fracture resistance. Nanoindentation, a widely used experimental technique for obtaining quantitative data on the mechanical properties of heterogeneous materials, addresses this need. This technique is particularly well-suited for characterizing material properties of individual phases within complex composite materials. Asphalt concrete is one example of a widely used complex heterogeneous composite material, with asphalt binder holding together aggregates with length scales ranging from microns to centimeters.

1.1. Asphalt binder and mastic

The chemistry of asphalt binder is highly complex, which has led to broad characterization based largely on functional groups, namely saturates, aromatics, resins, and asphaltenes, in order of increasing polarity. Pauli et al. [1] and De Moraes et al. [2] investigated the morphology of asphalt binders using atomic force microscopy (AFM). The "bee" structure, speculated to potentially be the result of crystallized paraffin waxes, forms the largest microstructure within asphalt binder's morphology. Typical bee sizes range from 2 to 8 μm, but can be significantly larger [1]. Not all binder microstructures, however, exhibit bee structures. De Moraes et al. [2] and Pauli et al. [1] demonstrate that the bee structure changes as a function of temperature. Pauli et al. [1] hypothesize

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that the interaction between crystallizing paraffin waxes and the remaining asphalt components is responsible for much of the morphological structuring of asphalt binder, including the bee structures.

A scale above the binder is the asphalt mastic, which is a mixture of asphalt binder and filler particulate matter no greater than 0.075 mm in characteristic length. Due partly to the relatively high specific surface area of mineral fillers compared to other particulates in asphalt concrete, some fillers are considered to be non-inert and chemically interactive with asphalt binder (e.g., hydrated lime, Portland cement), while others only have physico-chemical interactions and are referred to as inert fillers (e.g., granite, limestone). Binder and mastic are the two weakest phases of asphalt concrete, and effectively, all larger aggregates in asphalt concrete are coated with a thin layer of mastic [3]. Thus, the binder and mastic dominate viscoelastic and cohesive behavior of asphalt concrete and pose the most challenging constituent phases to characterize and model.

Hydrated lime fillers improve performance-related properties such as fracture resistance within an asphalt concrete mixture compared mixtures with normal mineral filler [4,5]. Hydrated lime modifies the surface properties of the aggregate, is highly chemically reactive chemically with the binder acids, and slows down the oxidative age hardening kinetics. The higher porosity of lime (due to Rigden air voids) explains its stiffening effect above room temperature [4].

1.2. Experimental characterization of adhesion and cohesion

The traditional methods for measuring surface energy components of asphalt binder are the Sessile drop test, which uses a goniometer to measure static contact angles of probe liquids with substrates [6], and the Wilhelmy plate method, a quasi-static method using a binder-coated glass slide suspended from a microbalance [7,8]. To our knowledge, the work of cohesion of mastics has not yet been reported in literature.

Past research on work of adhesion, cohesion, and surface energy at the microscale has focused on AFM experiments on binder. Little and Bhasin [9] and Pauli et al. [10] characterized adhesion in terms of the work required to detach a 5 μm cantilever-mounted glass bead from an asphalt thin-film surface after the application of various levels of rate-dependent external loading. Tan and Guo [11] used AFM and Fourier transform infrared spectroscopy to analyze binder-filler physicochemical interactions. Al-Rawashdeh [12] used AFM with functionalized tips to investigate the effects of water on the adhesive and cohesive forces in asphalt binders.

Further adhesion research has been conducted by Pauli et al. [13], who developed an adhesion energy test for force–displacement AFM based on fracture energy and crack propagation methods. Their technique involves creating and fracturing a standardized adhesive contact between asphalt and glass by application of a direct tensile force to the contact at various rates. It has been found that the rupture during pull-off always occurs within the thin film of binder between the probe and substrate. Hence, although the test is called an "adhesive test," the method is determining bonds that are cohesive in nature.

1.3. Nanoindentation on asphalt concrete

Most nanoindentation literature focuses on assessment of indentation modulus and hardness values derived from the Oliver–Pharr analysis method [14,15]. Jäger et al. [16] studied thermal effects on the viscoelastic properties of binder using the nanoindentation grid technique at low temperatures. Using a sharp tip, they demonstrated that a distribution of mechanical properties, with two primary responses, exists on asphalt binder surfaces. Tarefder et al. [17] developed a range of nanoindentation-derived elastic modulus and hardness values of aged asphalt. Tarefder and Faisal [18] examined the effects of creep hold time and loading rate on the mechanical properties of aged asphalt binder. They determined loading rates and hold times for binder that produced nanoindentation data, which they analyzed by the Oliver–Pharr method. No research has focused on deriving fundamental responses of neat, SBS-modified, and aged binder and mastic through cohesion testing in nanoindentation.

1.4. Research objectives and impacts for forensic investigations and multiscale modeling

Efforts to develop better analytical models for asphalt binder and mastic behavior are challenged by various aspects of the multiscale nature of asphalt concrete, including small length scales, nonlinear material behavior, high cohesion, high heterogeneity at multiple length scales, and significant complexity in experimental methods to measure properties at the smaller length scales. The study of the behavior of asphalt binder and mastic within asphalt mixtures is also a formidable challenge. Currently, forensic studies on asphalt binder within asphalt mixtures rely on solvent extraction and recovery to obtain asphalt binder specimens from laboratory-produced asphalt mixtures or field cores, which are then tested ex situ. These methods utilize solvents, heat, and centrifuge to separate asphalt from aggregate. Testing binder ex situ also prohibits assessment of cohesive and adhesive properties of the binder within asphalt concrete, which are influenced strongly by physicochemical interactions with aggregate.

These challenges motivate the primary advantages of using nanoindentation over any macroscale techniques, which focus on bulk, composite behavior. Improved characterization and modeling of asphalt binder and mastic as related to the overall bulk performance of asphalt concrete would enable improved material selection and engineering of binder and mastic and consequently allow for achieving superior pavement service life, durability, and resilience.

Therefore, the primary goal of this study is to characterize the cohesive properties, which are directly related to fracture resistance, of asphalt binder and mastic, using a new nanoscale technique. To accomplish this goal, low-load sphero-conical (blunt) nanoindentation experiments are conducted on Rolling Thin-Film Oven (RTFO) aged binders and mastics, with mineral and manufactured fillers and varying filler volumetric concentrations, to calculate and interpret cohesive properties as related to filler-dependent material performance. The nanoindentation experiments are conducted within a very small volume of material, opening up possibilities for future research in assessing in situ mastic properties within an asphalt concrete sample. Although soliciting small areas, nanoindentation tests are conducted using a tip of sufficient size to measure bulk binder and mastic responses.

2. Materials and methods

2.1. Materials

Two neat binders and one modified binder were considered in this study: a Performance Grade (PG) 64-22 North Carolina binder, a PG 70-22 binder, and a linear-grafted SBS (styrene–butadiene–styrene) modified binder. The thirty types of mastic used in this study were prepared using hydrated lime and granite filler in combination with PG 64-22, PG 70-22 and SBS-modified binders with varying filler dust-to-binder mass ratios (dust ratios) of 0.3, 0.6, 0.8, 1.0, and 1.2. These ratios were chosen based on the current Superpave volumetric mix design method, which includes a recommendation on the dust-to-binder mass ratio of 0.6–1.2 [19]. These mass ratios correspond to filler volume fractions in the range of 0.116–0.465 for granite and 0.111–0.444 for lime. At higher filler volume concentrations (ϕ), particle interactions dominate and mastic micromechanical theories become