Quantification of Aggregate-Binder Adhesion in Asphalt Mixtures Using Particle Probe Scanning Force Microscopes

Ting Tan, Yujie Li, and Jie Yang

***Abstract*—The adhesion between aggregates and asphalt binders is essential to the performance of asphalt mixtures. In order to quantify the aggregate-binder adhesion in microscale, the particle probe scanning force microscopes is created to measure the adhesion between aggregate minerals and various plain and modified binders. Average unit surface energy values showed that the alumina-binder pairs exhibited the largest adhesion. For the same control binder, the adhesion values increased as the weight percentages of selected modifiers increased. Morphologies of control and modified binders were characterized to reveal the microstructural variations of different binders. Statistical analyses were also performed to evaluate the effects of aggregate constituents on the aggregate-binder adhesion.**

***Index Terms*—Adhesion, Asphalt binder, Mineral Aggregate, Scanning Force Microscope**

I. Introduction

Hot mix asphalt (HMA) has been widely used as pavement materials for more than a century [1]. By 2015, there are over 457,000 km highway in China, and are over 658,000 km highway in US [2]. In 2012, the asphalt production in China exceeded 18 million metric tons. Large amounts of asphalt materials are also generated in US. Each year, approximate 4000 US companies produce more than 30 billion asphalt for pavement materials [2]. Despite these effort, it is estimated that only 50% main highways in US are in good condition, and 13% of them are in bad condition [3].

HMA is comprised of two important components, i.e., aggregates and asphalt binders. Aggregates are usually made of gradations of rocks and sands, such as limestone (primary calcium carbonate), granite (72.04 wt.% silica and 14.42 wt.% alumina), and sand (primary silica) [4]. Thus, the major chemical components of aggregate minerals include calcium carbonate, silica, and alumina.

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Asphalt binders are byproducts of the oil industry with complex chemical compositions. Based on the ASTM standard [5], asphalt binders can be classified into four major groups, i.e., asphaltenes, resins, aromatics and saturates. In order to improve the mixture performance, different polymers have been added to plain binders to modify their behavior [2], such as styrene-butadiene-rubber (SBR), styrene-butadiene-styrene (SBS) and polyphosphoric acid (PPA). The properties of asphalt binders, aggregates, and their interfaces substantially affect the performance of asphalt pavements.

There is a growing interest to study mechanical properties of asphalt materials using atomic force microscopes (AFM). For example, Tarefder et al. [6] measured the adhesion between plain silicon-nitride AFM tips and binders. Nazzal and Lana [7] used silicon-nitride AFM tips to investigate their adhesion to Advera, Evotherm, and Sasobit modified binders. These research provided important guidance to the study of adhesion and cohesion in asphalt mixtures. However, plain AFM tips are pyramids usually made from silicon or silicon nitride, and their tip radii are up to dozen nanometers. How to link nanoscale measurements to the crack initiation and propagation of asphalt mixtures in microscale remains a challenge. Meanwhile, the adhesion between the primary aggregate components and asphalt binders need to be quantified directly.

The objective of this paper is to use particle probe scanning force microscopes to quantify the adhesion between aggregate minerals and various modified binders at microscale. First, particle probes were created for scanning force microscopes using primary aggregate mineral spheres. Then, the aggregate-binder adhesion was measured between aggregate minerals and various plain and modified binders. Finally, statistical analyses were performed to elucidate effects of aggregate constituents on the aggregate-binder adhesion. This study focuses on the adhesion induced by intermolecular forces, while the interlocking mechanisms [8, 9] in adhesion are not considered.

II. Materials

A. Asphalt Binders

In this study, PG 64-22 binder (MRL, Austin, TX) were used as the control binders. PPA, SBR and SBS were added in 2 or 4 wt.% to prepare modifications. The PPA (ICL

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Performance, St. Lousi, MO) modifications were prepared by mixing the modifiers with the heated asphalt binder at 120˚C for 30 to 45 minutes. After that, the mixed binder was heated up to ~160˚C and maintained for 30 minutes to prepare substrates [2]. To prepare SBR modifications, SBR (Ultrapave, Dalton, GA) was added to the heated binder at 165˚C and mixed for 2 hours. To prepare SBS modifications, SBS (Bitumar, QC, Canada) was added into the heated control binder at 175˚C and mixed for 2 hours at 180˚C.

Thin film substrates were prepared for aggregate-binder adhesion measurements. Binders were stirred for 5 minutes before spead on a wafer of an area of 5 x 5 mm^2. The binder was gradually heated to 163˚C (325˚F) using a Model 11-300-49SHP ceramic hotplate (Thermo Fisher Scientific Inc., Waltham, MA), and a stainless steel spatula was used to spread the material. All binder specimens were then cooled to the ambient temperature, and stored in an oven at 30˚C overnight before measurements.

B. *Particle Probes*

Three types of particle probes were prepared to represent the primary minerals in aggregates, including the silica, alumina (Microspheres-Nanospheres Inc., Cold Spring, NY) and calcium carbonate (PlasmaChem Inc., Berlin, Germany). The mean diameters for these microspheres was ~6 µm.

A fabrication system is created to attach individual microsphere to tipless cantilever probes (NT-MDT Inc., Limerick, Ireland), and the details were described in prior studies [10, 11]. Typical spring constants of plain NSG11 probes are in the range of 2.5–10 N/m. The spring constants of particle-modified cantilevers were measured using the thermal tuning method [12-14].

III. Methods

A. *Scanning Force Microscopes*

Scanning Force microscopes (SFM) have been widely used for material characterization, including mechanical, chemical and magnetic properties. In the SFM system, a cantilever is used for force probing [15-17]. If the cantilever idea is maintained and the nanoscale AFM tip is switched to microspheres, forces in the order of micronewtons can be collected to quantify the adhesion between aggregate minerals and binder substrates. This is critical to the performance evaluation of asphalt mixtures since 1) adhesion between primary aggregate minerals and asphalt binders can be measured directly and 2) the adhesion measurements at microscale can be used as interfacial fracture criteria in multiscale aggregate-binder models that are based on images with the resolution of micrometers.

Figure 1 shows the basic parts of a particle probe scanning force microscope. During force probing, the particle probe is driven by bending the cantilever. In retracting, the microsphere does not disengage from the surface at the contact point because the adhesion keeps the microsphere in contact to the surface. The cantilever remains bent in the opposite direction until the restoring force overcomes the adhesion so the microsphere disengages from the surface.

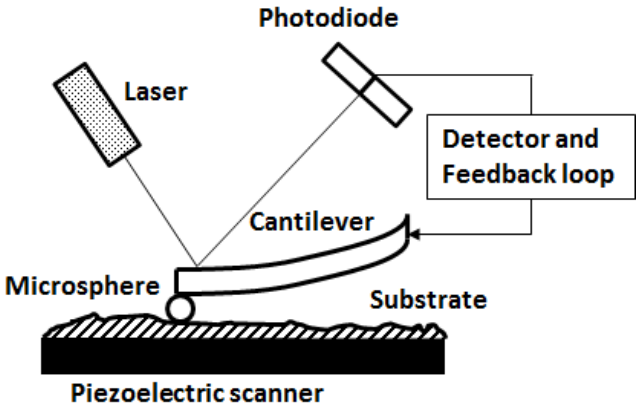

Fig. 1. A schematic of the particle probe scanning force microscope, consisting of the cantilever with a spherical probe at microscale.

The adhesive forces, F_{ad}, of the particle modified cantilever is given by the Hooke's Law that relates to the displacement described by

$$F_{ad} = k \cdot \Delta x \tag{1}$$

where k is the spring constant of the particle-modified cantilever, Δx is the separation distance between the tip-sample contact and the snap-off points.

B. *Unit Surface Energy*

The average surface energy per unit area, γ_{avg},, is calculated based on the Derjaguin-Muller-Toporov (DMT) [18, 19] model. DMT model has been applied to measure interactions between soft and hard materials [20], and used to characterize the adhesion of asphalt materials [21], which gives

$$\gamma_{\text{avg}} = \frac{1}{2}(W_{ad}) = \frac{1}{2}\left(\frac{F_{ad}}{2\pi R}\right) = \frac{F_{ad}}{4\pi R} \tag{2}$$

Where R is the radius of the contact particle, W_{ad} is the work of adhesion, and F_{ad} is the adhesive force between the micro-particle and the substrate.

C. *Design of Experiment*

A nanoscope E Scanning Force Microscope (Bruker Inc., Santa Barbara, CA) was used to measure the aggregate-binder adhesion for different aggregate minerals and binder substrates. Ten curves were collected at each location and three locations were selected on the same substrate, i.e., thirty measurements between one particle probe and one substrate. For each mineral-binder pair, replicas were produced using two particle probes and three substrates. Therefore, 180 data points were collected for each pair. The measurements were obtained at 25.7˚C and 30% relative humidity.

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IV. Results And Discussions

A. Particle Probe Scanning Force Microprobes

Particle probes were created by attaching individual spherical particles to microcantilevers. The resulting particle probes were checked using a scanning electronic microscope (JEOL JSM 6060 USA, Peabody, MA) to ensure the good quality. Figure 2 shows a representative probe with an alumina particle when the fabrication is complete. The sphere ensures ideal contact between the probe and binder substrate. Other probes had similar shapes and they were not shown here. The measured spring constants of different particle probe ranged from 2.2 to 5.6 N/m. The particle diameters ranged from 6.3 to 10.8 µm.

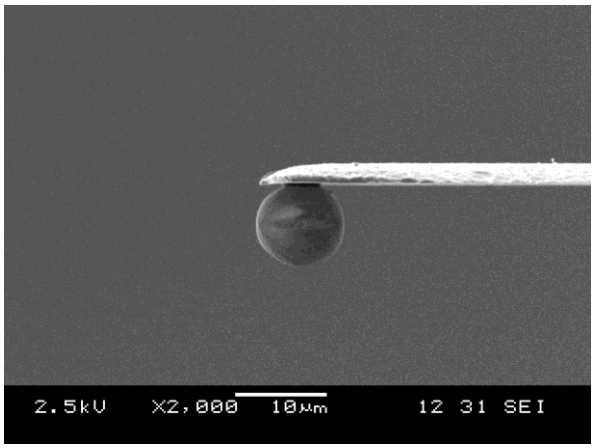

Fig. 2. An SEM image showing a particle probe made from an alumina microsphere and a microcantilever.

B. Adhesive Forces

It is critical to evaluate the adhesive force measured between microspheres and binder substrates. Representative adhesive forces between a calcium carbonate particle and a PG 64-22 binder substrate were shown in Fig. 3. The measured forces were on the order of micronewtons, which are much higher than those measured using plain AFM tips and binder substrates. This was because larger contact areas exited between the mineral particles and the binder substrates compared to those between the plain AFM tips and substrates. It is also observed that, for each particle-substrate pair, variations of adhesive forces were detected between replicas at different locations. This was probably because the probes contacted different phases of the binders. The adhesion variations between aggregate minerals and different binder phases will be studied in future work.

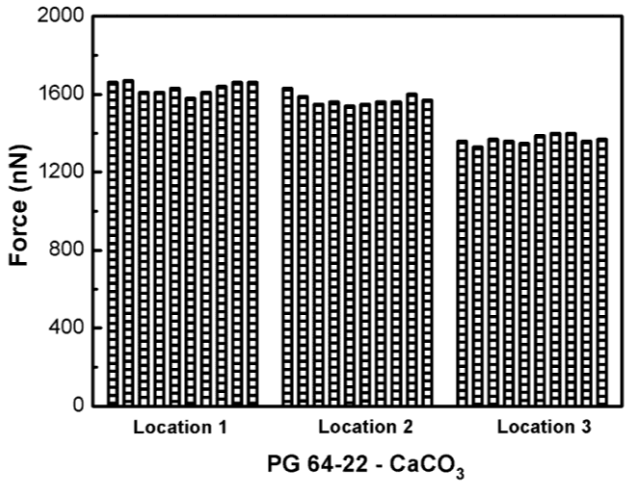

Fig. 3. Adhesive forces measured between a calcium carbonate probe and a PG 64-22 binder substrate at different locations.

C. Unit Surface Energy

Measurements of unit surface energy between aggregate particles and plain or modified PG 64-22 binders are shown in Figure 4. For each binder group, the largest unit surface energy values occurred between alumina spheres and binder substrates. The silica and calcium carbonate exhibited relatively lower adhesion values. For the same control binder, the alumina-binder adhesion increased as weight percentages of polymer modifiers (SBS) increase. However, no monotonic trends of adhesion between silica or calcium carbonate particles and modified binders were observed. These variations can be attributed to chemical properties of various aggregate minerals. Among these particles, alumina is the most polar, while calcium carbonate and silica are less polar [24, 25]. The resins in the binders are polar aromatic materials. Thus, stronger interactions were induced between alumina particles and binders compared to silica or calcium carbonate particles. Similar trends were observed in SBR and PPA modified PG 64-22 binders. These results showed that SBS, SBR, and PPA modifiers did affect the adhesion between binders and aggregate minerals.

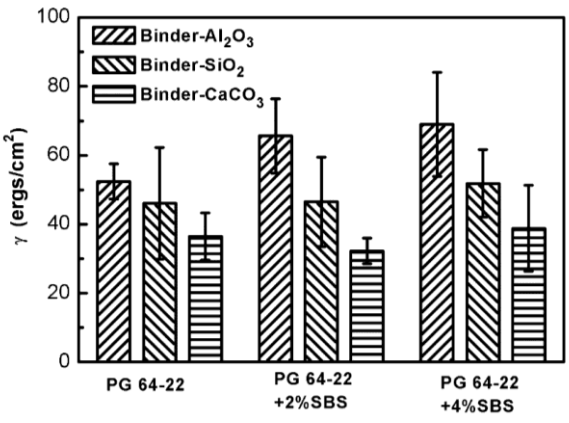

Fig. 4. Average unit surface energy between aggregate minerals and plain or SBS modified PG 64-22 binders.

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D. Binder microstructures

Surface morphologies of the plain and modified PG 64-22 binders are shown in Figure 5. The bee structures in the PG 64-22 binder are clearly detected by the amplitude scans (Fig. 5a), where rippling is aligned along the long axis of the small lenticular structures. For both 2 and 4 wt.% SBS modified binders (Figs. 5b and 5c), triangular tails beside bee structures were detected compared to those in control binders (Fig. 5a). For SBS modified binders, larger bee structures were detected in 2 wt.% SBS modified binders (Fig. 5b); while comparatively small and sparse bee structures were observed in 4 wt.% SBS modified binders (Fig. 5c).

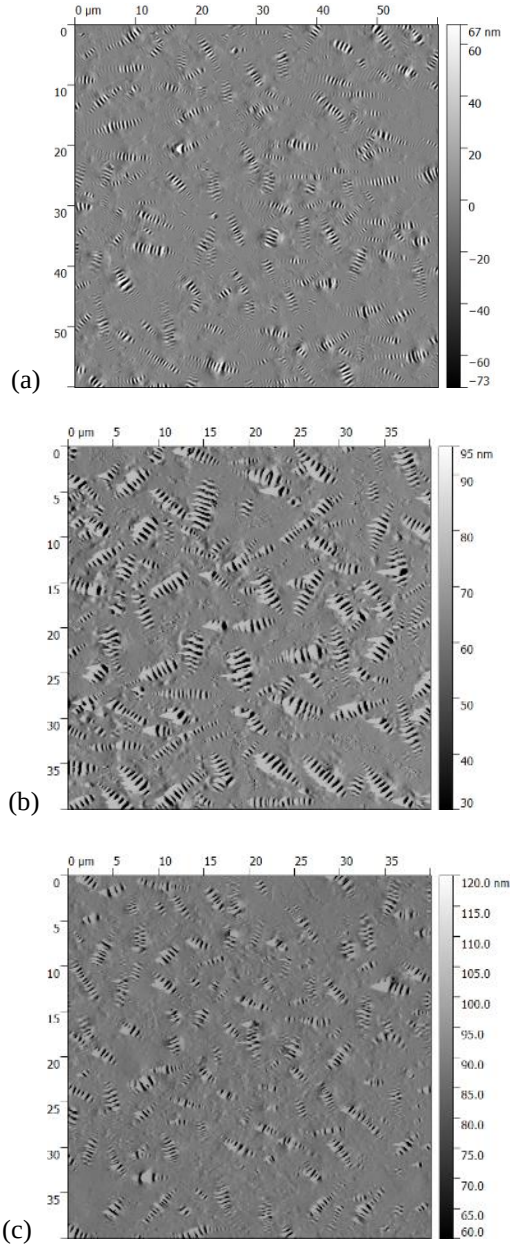

Fig. 5. Surface morphologies obtained through the amplitude scans for (a) controlled PG 64-22 binder; (b) 2 wt.% SBS modifications and (c) 4 wt.% SBS modifications.

E. Statistical Analysis

To evaluate the performance of particle probe method, the least squares analysis is performed to quantify to the effects of different aggregate constituents [26, 27]. The least squares means of adhesion (Fig. 6) exhibited that aggregate-binder adhesion was different between plain and modified PG 64-22 binders with various weight percentages of SBS. An exception was observed when the plain and 2 wt.% SBS modified PG 64-22 binders interacted with the silica microspheres. In general, the particle probe scanning force microscope is able to detect the differences between various binders.

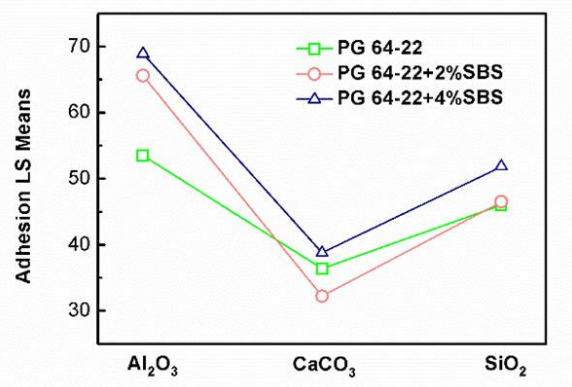

Fig. 6. Least squares means of adhesion measurements between alumina, calcium carbonate and silica microspheres and modified PG 64-22 binders with 2 and 4 wt.% SBS.

V. Conclusions

In this study, the particle probe scanning force microscopes were developed to quantify the adhesion in microscale between the aggregate minerals and plain and modified binders. Three types of particle probes were created using microspheres to represent the primary aggregate constituents, i.e., silica, calcium carbonate and alumina. Adhesive forces on the order of micronewtons were obtained resulting from the large contact between the microspherical probe and binder substrates. The average unit surface energy results showed that alumina-binder pairs exhibited the largest adhesion, while calcium carbonate- and silica-binder pairs exhibited relatively lower adhesion. This is because high polarity of alumina particles induced stronger interactions within alumina-binder pairs than within silica- and calcium carbonate-binder pairs. Morphologies of various modified binders revealed the correlation between the aggregate-binder adhesion and the binder microstructures. Finally the statistical analyses showed that the particle probe method is effective in quantifying the adhesion performance between various binders and aggregate minerals. The findings from this study could lead to the development of high-performance asphalt mixtures for pavement materials.

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