Observation of Asphalt Binder Microstructure with ESEM

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ABSTRACT

While there have been a several studies observing asphalt binder microstructure using the Scanning Electron Microscope (SEM) and Environmental Scanning Electron Microscope (ESEM), these have been few and far between. Thus, a procedure for the induction and identification of the microstructure has yet to be established. A suitable heat-sampling asphalt binder sample preparation method was determined for the test and a stainless steel sample holder developed. The magnification and ESEM settings conducive to observing the microstructure were determined through a number of observations. Both straight run binder (PG 58-28) and an air blown oxidized binder were analysed; their structures being compared for their relative size, abundance and other characteristics, showing a clear evolution in the fibril microstructure. It was confirmed that the fibril microstructure corresponded to actual characteristics in the asphalt binder. The results of this test will be used as the basis for a more comprehensive study on the ability of the ESEM to observe various asphalt binders, predict their rheological properties and performance-related parameters.

Keywords: ESEM, asphalt binder testing, microstructure, oxidation

1 INTRODUCTION

Asphalt binder is one of the most important pavement construction material in the world, with total global use estimated at 100 million tons per year, 85% of which is consumed by various kinds of asphalt pavement [1]. Nevertheless, due to the complicated nature of asphalt binder's source material in crude oil – being formed from organic matter under millions of years of heat and pressure [2] – there remains a lot to be known about its nature at a microscopic level. This understanding is especially important due to the changing nature of the way the bitumen is used in pavement [3]. The introduction of Polymer Modified Asphalt (PMA) [4], Recycled Asphalt Pavement (RAP) that incorporates aged binder [5] and the development of bio-sourced agents as both additives [6] and standalone binders [7], means that empirical approaches to binder are no longer always viable.

Asphalt binder contains thousands of hydrocarbons that form a colloidal system [8]. There have been several techniques developed to observe the nature asphalt binder microstructure, some of the most successful being Atomic Force Microscopy (AFM) [9] and Small-Angle Neutron Scattering (SANS) [10]. While AFM has been able to observe micelle structures associated with the n-paraffin waxes and the remaining non-wax maltene components [11], SANS was able to produce a model of the asphaltene structure.

Another microscopic technique with the potential to provide insight into the structure of asphalt binder is the Scanning Electron Microscope (SEM). The SEM irradiates the area of observation with a finely focused electron beam. Not only does this technique allow observation at very high magnifications, but it also allows for the identification of various sample properties, notably from the signals of secondary electrons (SE) and backscatter electrons (BSE) [12].

Although observations under SEM have shown indications of a microstructure in the asphalt binder [13]–[15], these studies have been sparse. The viscous and volatile nature of the binder presents certain issues when an electron beam is directed at the sample in high vacuum. Firstly, the use of the Energy-Dispersive X-Ray Spectrometry (EDS) attachment is limited due to the carbon atoms that flood the observation chamber from the efflorescence in high vacuum, severely altering the accuracy of the analysis. Secondly, the presence of vaporized carbon matter can present a serious issue for the vacuum pumps [16] designed for crystalline materials. Additionally, the viscous nature of bitumen makes it difficult to apply a conductive coating as is typically performed for SEM observation.

The Environmental Scanning Electron Microscope (ESEM) provides a viable alternative to SEM studies due to its ability to observe viscous oil bearing specimens at high vacuum. Specimens that exhibit volatility are less risky for the ESEM due to the relatively higher capacity of their pumps to handle volatile particles. Hawley et al. [17] and Rozeveld et al. [18] were able to observe "random networks of fibrils" in asphalt binder with the ESEM secondary electron signal. While the asphalt binder initially appears featureless – after several minutes of beam exposure – a network of fibrils or strands is observed. Although one may speculate that these network were merely the product of the electron beam, in subjecting the straight run moderate viscosity graded AC-10 samples (3x8mm) to tensile stresses. The authors found that the fibrils became well aligned with the direction of the stresses, indicating that the structures

– although induced by the electron beam – were clearly related to the binder microstructure [17], [18]. Rozeveld et al. reasoned that *"the beam volatilizes the low molecular weight oils in the asphalt by localized heating and thereby reveals the asphaltenes and resins after the upper surface layer oil has been removed"* [18].

Rozeveld et al. [18] and Stangl et al. [19] subjected the straight run and PMA samples to Thin Film Oven (TFOT) and Pressurized Aging Vessel (PAV) aging, which revealed an evolution in the fibril microstructure, especially from the PAV aging. Using image analysis, Stangl et al. found that the average fibril size was around 9 and 10 µm for straight and PMA binder, respectively. The fibrils became more robust after RTFOT aging (14 and 16 µm, respectively), and with PAV aging, reducing in size, while becoming much more numerous, organized and densely packed. The average diameters shrunk to 6 and 5 µm for straight run binder and PMA, respectively. The increase in packing density was correlated with an increase in the molecular weight of the asphalt binder, as what typically occurs during the asphalt aging process.

While there have been some promising results in using ESEM for the observation of asphalt binder microstructure, the studies have been few and far between as mentioned previously, with only two teams in the last 20 years performing relatively advanced work in this regard to the authors' knowledge. Additionally, a standard procedure for sample preparation and testing has not been established.

The objective of the current study is twofold. Firstly to validate the findings of [17]–[19] in observing asphalt binder under ESEM. In addition to observing the binder microstructure, the binder will also be subjected to aging to confirm that there is an evolution in the microstructure that is represented in the image. With the observation method validated, a procedure for sample preparation and testing will be established that takes into account binder heating, sample size, moulds, storage and ESEM settings. The ultimate goal of this study is to produce a protocol for ESEM sample preparation that can be easily reproduced by other laboratories and used towards renewed interest in this promising asphalt binder characterization technique.

2 MATERIALS AND METHODS

2.1 Asphalt Binder and Oxidation

The asphalt binder tested was an Imperial Oil Scona PG 58-28. The binder was oxidized by air blowing it at approximately 260°C in a lab scale air blower, with 50L/kg/min of air for a period of 5 h.

2.2 Sample Holders

In developing the sample holders, we need to think beyond the needs of the current study of binder observation under ESEM, along with its oxidation. Our goal is to ultimately develop the ESEM for a number of practical investigation that include the study of PMAs, RAP and binder blending. We must also consider the possibly of the integration of the sample with AFM and Dynamic Shear Rheometer (DSR) testing methods.

Firstly, the size and shape of the sample should not be too big to limit the quantity of binder in the ESEM chamber. While the ESEM is designed to handle volatile compounds like asphalt

binder, the quantity still should be limited, as microscopes are designed for small samples. In terms of the size and shape, the same dimensions were used as for the DSR moulds for "harder binders" (8 mm diameter and 2 mm height). The 2 mm depth is also not so deep as to prevent observation in AFM, where the samples are in contact with a small cantilever [9], and a high sample wall would be an obstruction. While it is not clear whether the AFM and DSR tests are viable for the same sample subsequent to ESEM observation, this leaves the option open for future studies.

For the sample holder materials, the DSR foam polymer was not used due to the deformation or damage that some foams can experience during vacuum like conditions [20]. Additionally, it is important to be able to heat the binder during sample preparation. Stainless steel was found to be compatible with the needs of both heating the sample on a plate, and observing them in the ESEM.

A stainless steel mould (Fig. 1) was prepared with a cylindrical opening 8 mm in diameter and 2 mm in height. The square perimeter of the mould was 10x10 mm and a 15 mm long handle was also added to be able to move it safely, with a 5 mm long base to ensure that the mould did not tip over.

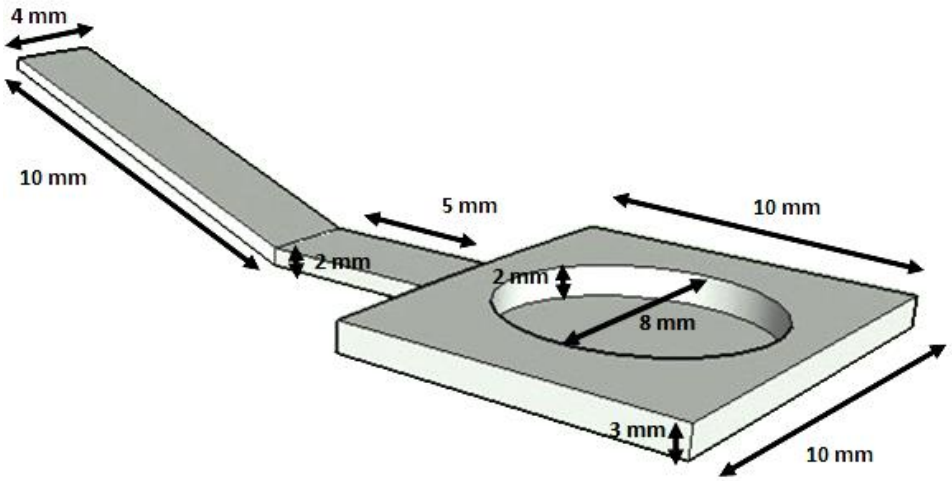

Figure 1 ESEM Stainless steel sample mould schematic

2.3 Sample Preparation

Although some AFM studies [11], [21] have relied on spin-casting for sample preparation, we wished to avoid dissolving the binder. A type of heat-casting was performed, as the binders were softened by heating them in an oven for approximately 1h at 110°C inside covered containers. Approximately 0.1 g was transferred from the containers into the sample holder with a spatula. The sampling was conducted under a fume hood to reduce the contamination of the sample by dust, which can happen very easily due to the sticky nature of asphalt cement [9], [16], [22]. The sample holder was place on a heater (at 150°C) for approximately 10s to flatten the sample and stored in covered plastic containers in a cooler with an electric fan to maintain the temperature at approximately 8°C.

2.4 ESEM Observation

The ESEM used was a FEI Quanta 250 FEG, with the EDS attachment removed since we did not require it. The observations (Fig. 2) were conducted in low vacuum mode under room temperature immediately after being removed from the cooler. The settings for microscope were an acceleration voltage of 20 keV and a chamber pressure of 0.8 mbar as in [23]. A lower acceleration voltage of 10 keV was tried, but the images were found too dark and required a longer observation time to produce the microstructures.

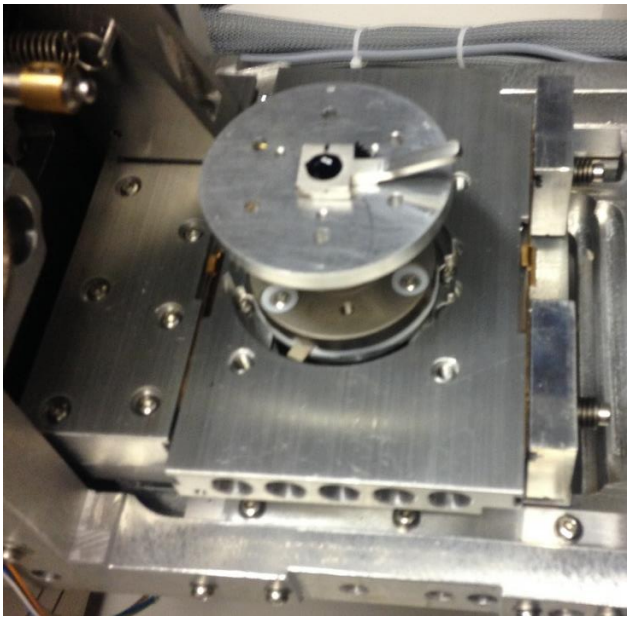

Figure 2 Stainless steel sample mould with binder in ESEM stage

3 RESULTS

3.1 Asphalt Binder under ESEM

A sample of PG 58-28 asphalt binder was observed inside the ESEM. It took approximately 10-15s for the binder to go from flat and featureless to having a visible fibril structure and took another 30s to stabilize. The structure was visible in both SE and BSE modes (Fig. 3). A magnification of 1000x was found to provide a good overall view of the structure. The fibril size was relatively large at around 15-20 µm, but the structure itself was relatively sparse. Both the SE and BSE modes provided a clear image, but the SE mode image showed more depth. The structure was consistent throughout the sample and the fibril was similar to that found for unaged straight run asphalt binder in [16], [18], [23], as they also found relatively large and sparse fibrils.

The sample holder was adequate for the testing. The quantity of binder (less than 0.1g) did not appear to pose a problem for the ESEM. It is worth noting that the height of the handle did require the beam source to be 20 mm away from the surface of the sample as opposed to the typical 10 mm, although this did not appear to be detrimental to the analysis. There was also an issue with the binder sticking to the stainless steel, which could be mitigated by using a non-stick material. Additionally, there was a significant presence of dust in some parts of the sample, indicating that the sample preparation could be improved.

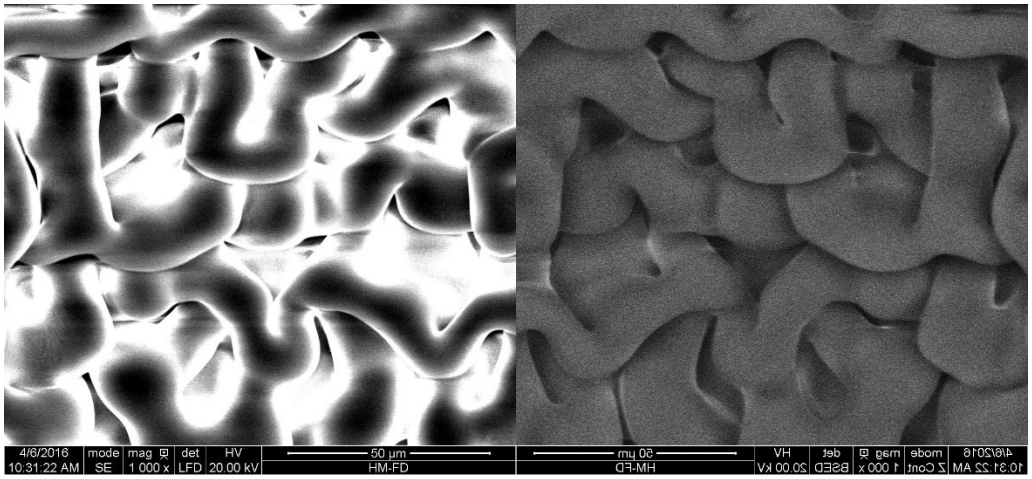

Figure 3 ESEM Images of 58-28 binder with SE (left) and BSE (right) modes at 1000x magnification

3.2 Asphalt Binder Oxidation under ESEM

In order to determine the validity of the analysis method, an oxidized 58-28 asphalt binder sample was compared to a normal one. The resulting images (Fig. 4) clearly showed an evolution in the fibril structure compared to the unaged sample in Fig. 3. As observed by [18], [19] after TFOT+PAV aging, the size of the fibrils became smaller (6-9 µm) and the structure became denser and more intertwined. The structure also appears to be much more perpendicular and predictable.

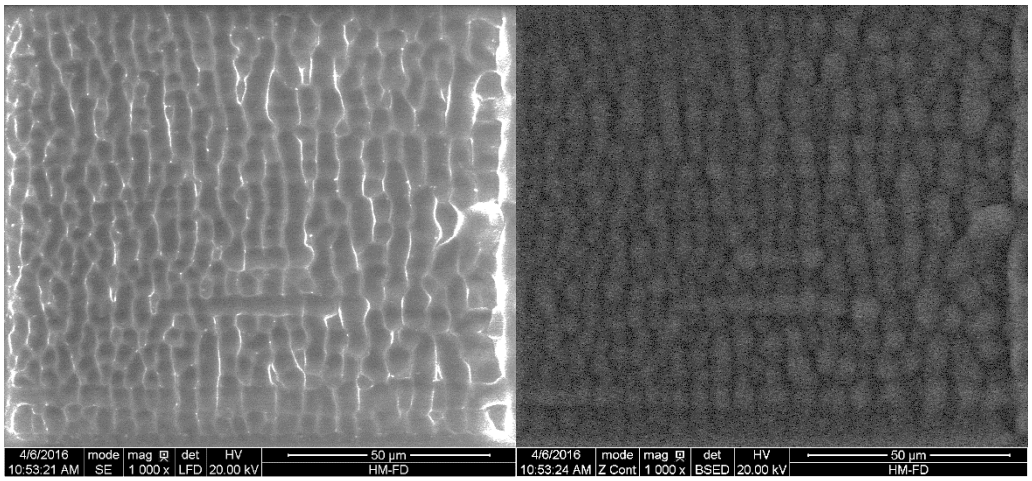

Figure 3 ESEM Images of oxidized 58-28 binder with SE (left) and BSE (right) modes at 1000x magnification

While the fibril structure observed in this study is indeed induced by the electron beam, the modification of the structure clearly shows an evolution in the binder microstructure. Furthermore, the evolution of the structure into a more dense and intertwined network of fibrils is consistent with the physical binder hardening observed during oxidation [24]–[26].

While the electron beam is involved in provoking the fibril structures we observe in the ESEM images, the current study, along with the tensile testing in [17], [18], suggest that this corresponds to actual characteristics in the binder. Given that the asphalt binder microstructure is still a relative "black box" in terms of understanding compared to other construction materials, the observation of the binder under ESEM is a promising analysis technique that can be a useful tool in the analysis of asphalt binder aging, blending, addition of modifiers, dissolution and other aspects.

4 CONCLUSIONS

This paper presented a laboratory study on the potential of the use of the Environmental Scanning Electron Microscope for the observation of asphalt binder microstructure. A final procedure for the induction and identification of the microstructure has yet to be finalized and the following conclusions have been drawn:

- The observed fibril microstructure is consistent and visible over an entire sample in both SE and BSE modes. The oxidation of the asphalt further confirmed that the fibril structure was related to real changes in the binder as it evolved with oxidation. The results were consistent with previous research on binder performed using the ESEM.

- The binder preparation technique was adequate, although improvements could be made with more dust control. Additionally, the sample holder could potentially be made with a material that does not adhere to binder.

- The ESEM has been validated as a tool for the observation of the binder microstructure that could be developed further with the observation of aging, PMAs, binder blending and other aspects.

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