RILEM Technical Letters (2017) 2: 10-13
DOI: http://dx.doi.org/10.21809/rilemtechlett.2017.31

Preparation of field samples and characterization of the microstructure of bituminous materials as displayed in field samples by AFM measurements

Hartmut Fischer[a*], Sayeda Nahar[b]

[a] TNO Materials Performance
[b] Delft University of Technology, currently Latexfalt B.V.

Received: 09 June 2017 / Accepted: 09 August 2017 / Published online: 21 September2017

Abstract

The properties of asphalt concrete depend strongly on the interaction between binder and fillers/aggregates. Especially the development of microstructures of the bituminous binders employed and the interaction of the different parts of the microstructure with the solid surface of the filler particles are important parameters in determining the long-term performance of these materials. This paper describes a procedure for the preparation of an extracted field sample to be accessible for micro-structural investigations by atomic force microscopy and the results of such experiments.

Keywords: Bitumen; Asphalt; filed samples; AFM; Microstructure

1 Introduction

Asphalt based pavements based on natural bitumen were explored in the 19th century in European towns (Paris 1838, London 1869) and since then extensively adopted [1]. Today, most the pavements in Europe are constructed with asphalt concrete materials derived from synthetic bitumen obtained as the vacuum residue of Petroleum distillation and this will be also remaining the material of choice for the near future.

The films of bitumen between aggregate particles in an asphalt mixture are generally thin, the average thickness of the films is not more than a couple of micrometers at the most 10 depending on the asphalt composition [2]. The primary function of bitumen in pavements is to act as adhesive with the purpose to provide a bond between different particles. Recent investigations on a micro or molecular scale show, that especially asphaltenes preferentially wet the aggregate surfaces [3, 4]. The most probable reason for the preferential wetting of interfaces by asphaltenes is that the amount of adhesion between bitumen and the aggregate surface is not entirely enthalpy determined and related to the suspected polarity but is also entropy related. It is certainly entropically more favorable for the whole thermodynamic system: bitumen-aggregate surface to adhere a small number of large, planar molecules than many small molecules. In summary, the overall free energy of the system is governing asphaltene molecules towards the solid surface.

2 Microstructural considerations

Investigations on the spontaneous formation and behavior of distinct microstructures (as noticed before by several researchers) performed by the authors has shown that these structures are universally present in the binder material (Fig. 1) independent from the source (origin) or the grade of the bitumen [5] except non-waxy binders (Nynas) which show micro-phase separation but no microstructural features.

Also, a reversible change in the microstructure with increasing temperatures has been reported [6, 7]. Furthermore, the identified different phases vary in physical state (at different T) and different chemical compositions [8]. Because of the interaction with the solid aggregate surface, where preferentially asphaltenes are absorbed, the composition of the different phases in the 'bulk' of the bitumen in asphalt concrete may differ from the phase structuring as present in virgin bitumen. So far it is not known whether this is the case and what the consequences are to the formation of the earlier mentioned unique microstructures (catana/peri and perpetua phase) and consequently to the micromechanical properties of the binder in a *mastic* system [5, 9].

---

* Corresponding author: Hartmut Fischer, E-mail: hartmut.fischer@tno.nl

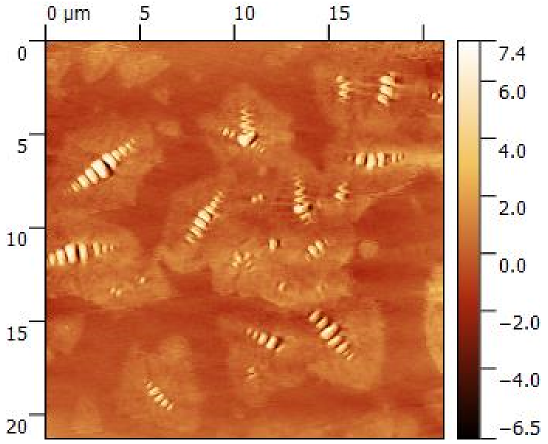

Figure 1. Typical AFM phase contrast picture of well developed micrustructures within a bitumen binder showing the peri (bee) and perpetua phase and cystalline features of the peri phase [5].

3 Outline

This communication focusses on methods to directly access structural information present within á asphalt *mortar* as present in a road sample (Porous asphalt Concrete - PA) as this has not been performed so far. The binder will *not* be chemically extracted from the mastic and subsequently inspected as in all existing studies (hence no earlier reports on direct studies of a mastic has been found) but thermally stimulated to generate suitable surfaces from the actual asphalt sample for micro inspection via Atomic Force Microscopy - AFM. Asphalt concrete samples are notoriously difficult to image by AFM to reveal microstructural features due to difficulties in creating smooth surfaces for AFM measurement purposes. Most of the AFM's can only coop with a height range in their scan size of a maximum of 10 microns or less. Even after cutting of a suitable sample and polishing the cut surface at low temperatures, the binder between the aggregates and filler particles remains highly viscous and will flow to an extent that the surfaces are not suited for AFM inspection and the much harder filler particles will remain as obstacles for the inspection. Therefore, it was needed to develop an experimental procedure to gather some sort of micro-structural information from such samples without using solvents etc. to separate the binder from aggregates and fillers and create smooth enough surfaces to be used in AFM measurements.

4 Materials

A road sample (150 mm core) of a porous asphalt concrete (PA) wearing course was used to create the material under investigation. The core was extracted from a wearing course on a highway in the Netherlands, form a position in the middle of a traffic lane, between the wheel tracks. The PA material was a PA with a maximum aggregate size of 16 mm, binder content of approx. 5.2 % and with a void content of about 20%. The core was cut into smaller samples for further processing.

5 Preparation methodology

First attempts to cut the sample to obtain flat surfaces and to polish them were partly successful. The viscoelastic nature of the binder (it still flows), resulted in a height differences of the mastic (i.e. surface roughness) compared to the aggregates. Hence, the steepness of the slopes of the sample's surface turned out to be too steep to analyze these surface with the AFM. Therefore, a different method of preparation and investigation was explored and developed.

Firstly, small slices of the PA were cut (dimensions 1x1.5x2 cm) and pre-polished (Fig. 2a). Subsequently, theses samples were embedded in epoxy matrix for fine polishing (Fig. 2b). However, even after polishing, and mainly due to the differences in mechanics/hardness of the filler particles and of the bitumen binder, substantial height differences between both parts as detected during scanning using the AFM were present. Therefore, theses samples were annealed at 90°C for 1 hr. in an oven. Consequently, the mastic (bitumen binder together with filler particles incorporated) became again highly viscous and could partially flow out (due to the action of the included air in the pores of the ZOAB sample) onto the epoxy, now covering partly the embedding epoxy and the polished aggregate and suitable for inspection using the AFM (Fig. 2c). However, it is expected that the *principle* micro-structure of the mastic is not altered since the temperature used is just below the last by DSC recordable transitions, hence complete melting did not occur [6]. Higher temperatures as e.g. applied for a simple melting out would truly erase ***all*** microstructural features and also the effect of the closeness of the interfaces of the filler particles onto the microstructure, which is just the point of interest. Also, due to the strong interaction of parts of the binder (asphaltenes in the bitumen) with the surfaces of the filler [3], a modification of the interface by the heating is not very likely. Trials performed at lower temperatures did not change the initially observed height differences between filler and binder, higher temperatures lead to a complete melting of the structures within the binder phase and to a disappearance of the crystals within the binder (micro-structure) and are consequently not suited for an investigation of the structures present in an asphalt road sample. Such crystalline structures are known to form only after long annealing at elevated temperatures (> 60 °C, days).

6 Results

Several different areas of the bituminous binder of the annealed sample were inspected using a EasyScan2 AFM (NanoSurf AG Switzerland) and XYNCHR probes (Nanosensors). All AFM figures shown are topological images as well as the corresponding phase contrast images.

Due to the thermal annealing step, it was possible to image reasonably flat areas of the mastic/binder while using the AFM. Clearly, the presence of large mineral filler particles is observed, as can be seen in Fig. 3a and 3c in the topography images.

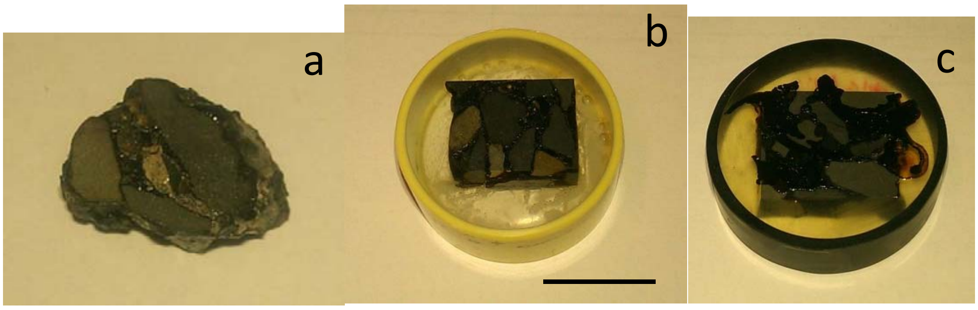

Figure 1. *a)* original piece of ZOAB; *b)* embedded piece of ZOAB; *c)* out flow of bitumen onto the flat polished epoxy matrix. Scale bar 2 cm.

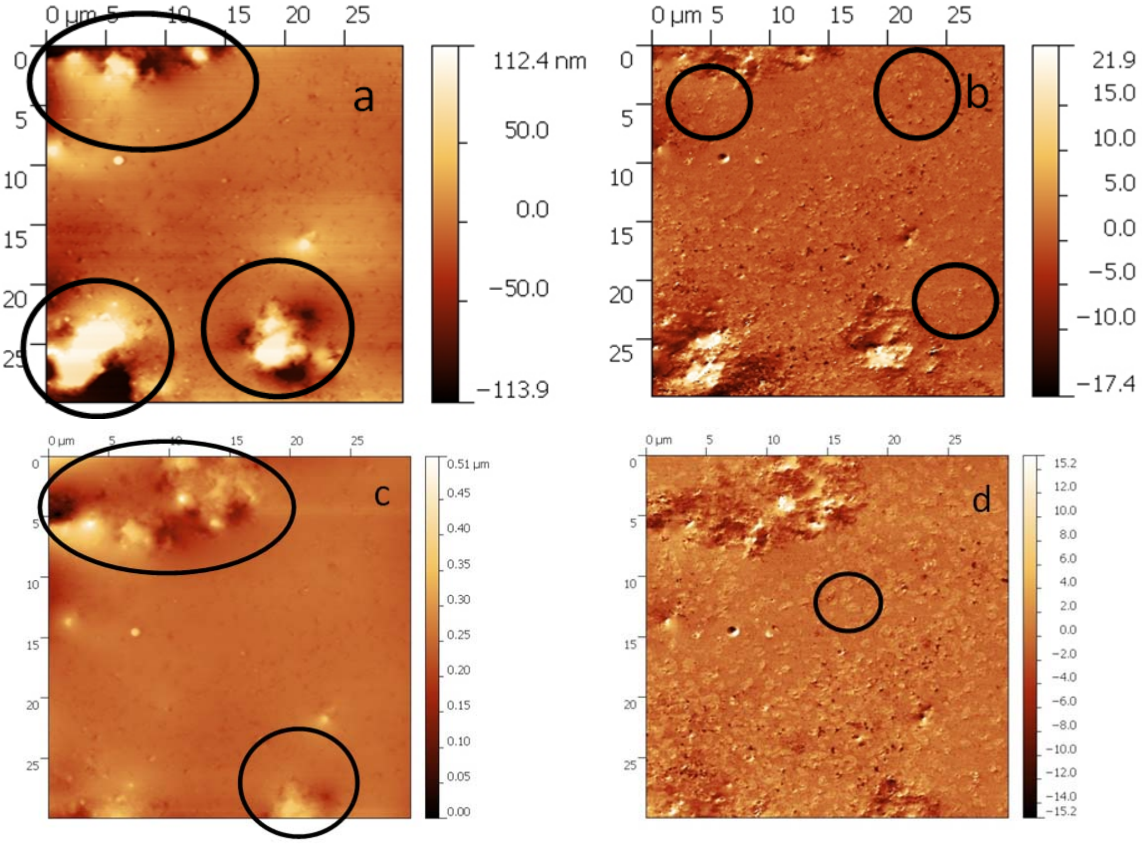

Figure 3. Height (a,c) and phase (b, d) contrast pictures as recorded by AFM of the asphalt sample under investigation (AFM imaging procedures are descibed in [5-11]. The height images show the presence of filler particles (encircled). The phase contrast images show clearly the presence of two phases within the binder (peri and perpatua phase) and especially the crystallites and bee-like features (encircled) within the peri phase [12].

The phase contrast images recorded are better suited to identify the presence of the catana/peri phase and of the perpetua phase and to distinguish between them due to the differences in mechanics as reported earlier [10,110]. The catana/peri phase displays leaf-like crystals (bright, indicating a higher modulus) and occasionally “bee” structures (Fig. 3b, d and 4b).

Furthermore, spiral crystal features typically for the appearance of crystalline waxes are observable (Fig. 5).

7 Conclusion: Preparation of field samples and AFM measurements of field samples

Field samples are fundamentally different from plain bituminous binders since they compromise the whole complexity of the combination of binder, filler and aggregates. The intention was an evaluation of the possibility to image displayed microstructures without solvent extraction of the binder and tedious separation processes. For this purpose, a sample has been extracted from a pavement material, cut and polished and heat treated following the protocol for AFM investigations of microstructures of bituminous binders. However, the binder will not separate completely from the filler particles, so an image may and will contain filler particles.

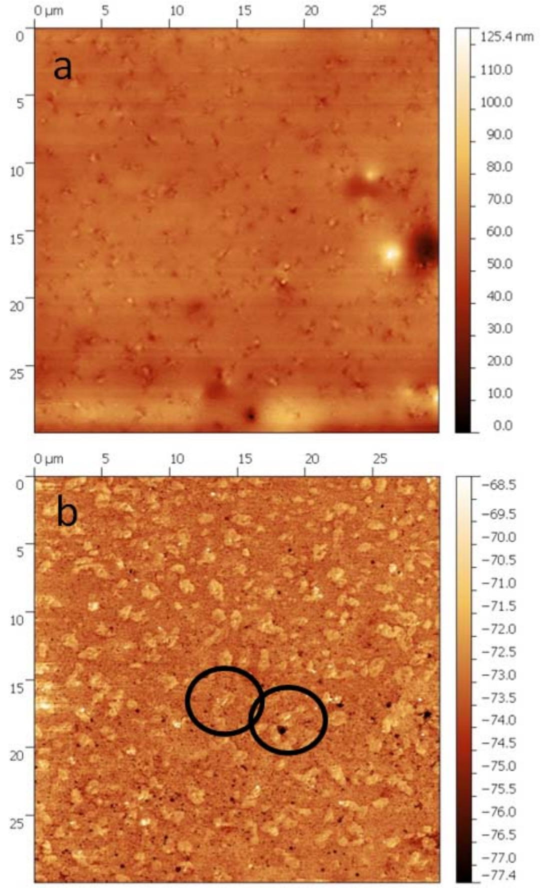

Figure 4. Height (a) and phase (b) contrast pictures as recorded by AFM of the binder part of the asphalt sample under investigation. The phase contrast image shows clearly the presence of crystals with bees inside in the circles (peri phase) within a continuum of perpetuum phase [12].

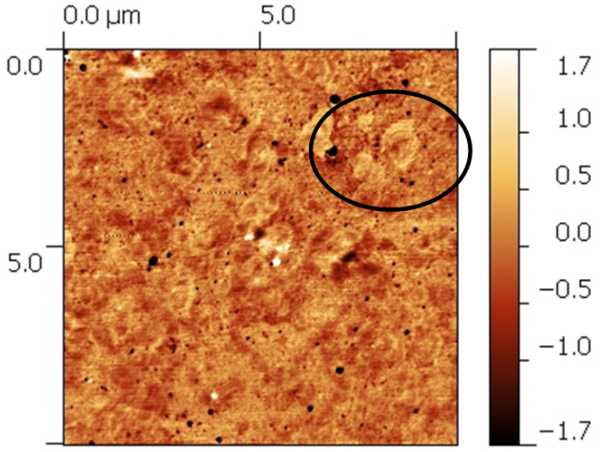

Figure 5. Phase contrast image of the binder part only showing spiral crystal features in the circle (peri-phase).

Using this technique, it is possible to image the microstructure of bituminous binders in asphalt. The experimental results show the presence of the (crystalline) peri-phase and of the continuous viscous perpetua phase. Additionally, "bee's" or catana-phase can be observed in the center of the peri-phase. Hence, it can be concluded that the binder in asphalt displays the same microstructural features as the plain binder.

Acknowledgements

The work presented in this article is the result of cooperative efforts in the InfraQuest project IQ-2012-49 "AFM on Bitumen'.

References

[1] J. Murali Krishnan, K.R. Rajagopal, Review of uses and modeling of bitumen from ancient to modern times. Appl Mech Rev (2003) 56: 149–214. https://doi.org/10.1115/1.1529658

[2] M.A. Elseifi, I.L. Al-Qadi, S.-H. Yang, S.H. Carpenter, Validity of asphalt binder film thickness concept in hot-mix asphalt. Transp Res Rec J Transp Res Board 2057 (2008): 37-45. https://doi.org/10.3141/2057-05

[3] J.M. Létoffé et al. Caractérisation de l'interaction bitume-agrégat par microcalorimétrie isotherme. Thermochimica Acta (1992) 210: 27-40. https://doi.org/10.1016/0040-6031(92)80274-Z

[4] H.R. Fischer, E.C. Dillingh, C.G.M. Hermse, On the interfacial interaction between bituminous binders and mineral surfaces as present in asphalt mixtures. Applied Surface Science (2013) 265: 495-499. https://doi.org/10.1016/j.apsusc.2012.11.034

[5] H.R. Fischer, S.D. Mookhoek, A study of the influence of the microstructure of one type of bitumen grade on the performance as a binder. Constr Build Mater (2016) 117: 1-7. https://doi.org/10.1016/j.conbuildmat.2016.04.129

[6] H.R. Fischer, E.C. Dillingh, C.G.M. Hermse, On the microstructure of bituminous binders. Road Materials and Pavement Design (2014) 15: 1-15. https://doi.org/10.1080/14680629.2013.837838

[7] S.N. Nahar, A.J.M. Schmets, A. Scarpas, G. Schitter, Temperature and thermal history dependence of the microstructure in bituminous materials. European Polymer Journal (2013) 49: 1964-1974. https://doi.org/10.1016/j.eurpolymj.2013.03.027

[8] H.R. Fischer, A. Cernescu, Relation of chemical composition to asphalt microstructure - Details and properties of micro-structures in bitumen as seen by thermal and friction force microscopy and by scanning near-filed optical microscopy. Fuel (2015) 153: 628-633. https://doi.org/10.1016/j.fuel.2015.03.043

[9] H.R. Fischer, B. Dillingh, Response of the microstructure of bitumen upon stress–damage initiation and recovery. Road Materials and Pavement Design (2015) 16: 31-45. https://doi.org/10.1080/14680629.2014.960884

[10] H.R. Fischer, H. Stadler, N. Erina, Quantitative temperature-depending mapping of mechanical properties of bitumen at the nanoscale using the AFM operated with PeakForce TappingTM mode. Journal of Microscopy (2013) 250: 210–217. https://doi.org/10.1111/jmi.12036

[11] S. N. Nahar, A. J. M. Schmets, G. Schitter, A. Scarpas, Quantitative nanomechanical property mapping of bitumen micro-phases by peak-force Atomic Force Microscopy. Asphalt Pavements (2014): 1397 -1406. https://doi.org/10.1201/b17219-169

[12] S. N. Nahar, A. J. M. Schmets, A. Scarpas, G. Schitter, Temperature and thermal history dependence of the microstructure in bituminous materials. European Polymer Journal (2013) 49: 1964-1974. https://doi.org/10.1016/j.eurpolymj.2013.03.027