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Investigation of the bulk and surface microstructure of bitumen by atomic force microscopy

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HIGHLIGHTS

- AFM measurements, on air-cooled surfaces, can reveal Bees.
- Bitumen with a larger melting enthalpy tend to have more Bees.
- Bee structures shapes and sizes divert, although a constant unit cell is observed.
- Fracture surfaces did not reveal any Bee structures.
- Reheating a fracture surface of a wax containing bitumen results in bee structures.

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ABSTRACT

Bitumen, the heavy residue of crude oil, can display a rich microscale morphology, including so-called Bee structures. The use of Atomic Force Microscopy (AFM) measurements in literature strongly indicates that the appearance of Bee structures is related to the presence of paraffin wax crystals. Most studies have investigated standard bitumen surfaces when cooling bitumen in an air atmosphere. Only a few investigations have analysed surfaces formed in other media or have analysed fractured surfaces which relate to the bulk morphology. Although considerable research has focussed on identifying Bee structures, less attention has been paid to the Bee structure morphology of different bitumen types and the relations to other binder parameters. The comparison between the micro morphology of the air-oil interface compared to the bulk phase volume has been studied even less.

In this experimental study, five bitumen samples were selected based on differences in their natural wax content. Both the air-cooled surface interface and fractured surfaces were characterised using AFM in tapping mode. All the air-cooled surfaces revealed Bee structures, except the wax-free bitumen, which did not display the presence of any Bee structure. None of the fracture surfaces revealed Bee structures. Reheating a fractured surface of a wax-containing bitumen transformed the morphology into Bee structures.

The experiments demonstrate that Bee structures are present in different binders but display very different shapes and sizes. However: image analysis indicates that the unit cell inside these structures is rather constant and independent of the binder type. This work confirms a relationship between natural wax and Bee structures and it also shows that Bee structures, as such, are a surface phenomenon which is not present in the bulk phase volume of samples.

1. Introduction

Bitumen, obtained as the residue from crude oil after distillation, has excellent waterproofing and binding properties and is an important component of our asphalt pavements. Chemically, bitumen consists mainly of hydrocarbons, including saturated and aromatic structures, which can be arranged in many different configurations. In addition, small percentages of sulphur, nitrogen and oxygen, and traces of vanadium, nickel, magnesium, iron and calcium can be present [1]. Although the general elemental composition of bitumen and the type of functional chemical groups are

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well established, there are still a lot of uncertainties with regard to the microstructure, ranging from a colloidal system, in which asphaltenes are dispersed in a matrix of maltenes, to an almost single-phased material. And, there is still a large gap in understanding the relations between the chemical, microstructural and mechanical properties [2–4].

The characterisation of surface structures on a nanoscale level became possible with the development of the atomic force microscope (AFM) in 1986 by Binning et al. [5]. Loeber et al. [6,7], one of the first authors showing AFM images of bitumen. These images revealed rippled microstructures represented by yellow and black strips, which were referred to as ‘‘Bees” by the author. In these initial studies, Bee structures were concluded to be a structuring of asphaltenes. Further evidence for this conclusion was provided in literature. In 2001, the group of Pauli et al. [8] investigated Bee structures after doping bitumen with extra asphaltenes. An increase in the concentration of asphaltenes could be related to an increase in the density of Bee-shaped microstructures on the bitumen surface. Jäger at al. [4] observed Bee structures on the surface of asphaltenes, while no such structures could be detected on maltene surfaces. Masson et al. [9], studied 13 bitumen types, and in this study, no correlation between the AFM morphology and the four components analysis of bitumen into saturates, resins, aromatics and asphaltenes could be indicated.

Depending on the mode of measurement – tapping versus pulsed-force mode – AFM not only provides insight into the surface topography but can also asses differences in stiffness and adhesion properties on a nanoscale level. This technique allowed to relate differences in topography on a bitumen surface to differences in mechanical and adhesive properties [10–16]. Jäger et al. [4], for example, identified four different material phases at the bitumen-scale with different topography and stiffness properties. In his paper the bitumen surface was cooled during the experiments, using a Peltier element. There was also a long-time delay of 7 days between sample preparation and testing.

Bee structures have also been related to a crystallization of natural wax and several studies [17,18] have provided strong evidence for this. For example, the RILEM technical committee 231 on nano bituminous materials, applied AFM at different temperatures for different types of binders and could correlate the changes in the Bee structures to signals in differential scanning calorimetry (DSC) measurements [19–21]. Moreover, tests demonstrated that a wax-free bitumen did not reveal any type of structure. Bee structures appeared on the surface only after adding commercial waxes to this bitumen. Regarding the mechanism why Bees are formed, Asa Laurell Lyne made a significant contribution [22]. She proposed a mechanism based on the solid-liquid phase separation and differential contraction of paraffin wax crystals during cooling from the hot liquid state, Because of differences in the elastic modulus of the wax compared to the matrix, this leads to a wrinkling of the surface. The assumption that the rippled surface morphologies are paraffin wax crystals in a strained configuration was also put forward by Pauli et al. [23]. Fischer and Cernescu [24] also supported this conclusion.

In addition, many studies also revealed that AFM images are highly dependent on the thermal history, sample preparation and analysis conditions [25–29]. Nahar et al. [30] illustrated that, in addition to the particular binder type, parameters such as the thickness of the sample, heat treatment temperature and duration, play an important role in the size and shape of the Bee structures. The exposure of bitumen films to other media, such as water, also influences the microstructures, including the topographical and mechanical properties. It was shown that increasing exposure times to water flattens out the difference in surface height [31]. In the work of Hung [32], samples exposed to water at ambient temperature showed the formation of ‘‘nano-bumps”. It was hypothesized that these nano-bumps are absorbing water and seeping up from underneath the Bee structure. The valleys of the Bee structure as well as the interfaces contain material with different mechanical properties from the surrounding surface.

A few studies have investigated the microstructures in the bulk state of the binder. Fischer, Dillingh, and Hermse [33] and Yue Hou [34] performed AFM tests on both the surface and the bulk. These experiments showed Bee structures only on the surface. In the bulk phase circular structures were observed, these became more obvious when scanning acoustic microscopy was applied. In this research, the bulk phase was evaluated by means of the fracture surface, which was prepared after freezing (−20 °C) the sample followed by a brittle fracture. The AFM measurements were performed at room temperature.

In this study, the AFM technique is applied to a set of bitumens from different origins and differing in the natural wax content. This should enable one to observe the formation of Bee structures and possibly to confirm relations between these bee structures and the presence of natural wax or other binder parameters. Secondly, the same binders are evaluated in the bulk structure by means of preparing fracture surfaces to investigate what type of microstructures can be formed in the bulk phase. Finally, a fractured surface is reheated and evaluated.

2. Experimental part

2.1. Experimental setup

2.1.1. Atomic force microscopy (AFM)

Atomic-force microscopy (AFM) is a technique based on the interaction between the sample and a tiny probe, called the cantilever (Fig. 1) [5].

The cantilever holds a sharp tip, which is the actual part that interacts with the sample surface. By scanning a sample surface and plotting how these interactions change in function of the x-y position, an image can be obtained which plots several physical properties such as, e.g., the sample roughness. The basic working principle of AFM is that a sharp tip attached at the end of a cantilever, probes the specimen surface with a laser beam focused at the end of the cantilever reflecting into a photodetector to track the surface topography.

Tapping-Mode AFM, is a high-amplitude dynamic mode where an amplitude modulation feedback is used to image the sample topography [35–39]. The cantilever-tip ensemble is oscillated at a frequency close to its resonance frequency. This oscillation of the cantilever is triggered by the distance between tip and sample surface. During the sample scan the oscillation amplitude is kept at a fixed value. This can be obtained by varying the Z axis, height, using a feedback loop. Catering the Z axis data for each point during scanning results in a high-resolution imaging of surface topography [40]. Although the Tapping-Mode offers advantages when measuring low viscosity samples, other AFM techniques with diverse imaging modes for microscopic characterization of different phases, mechanical properties and other phenomena of various materials exist [45,46].

2.1.2. AFM instrumental settings

The measurements were performed using the AFM [44] setup available at the Physical Chemistry and Polymer Science (FYSC) [41] the parameters used are presented in Table 1. All AFM scans were performed using tapping mode in air and at room temperature 20 °C. In this case an AC 160 TS silicon cantilever [47] tip is used. This measuring probe is a piece cut from a Si wafer, and a tiny cantilever is formed on it. The back side of the cantilever has a reflective coating to increase the laser signal as well as to protect