



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-field optical microscopy



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HIGHLIGHTS

- Relationship between asphalt microstructure and material characteristics investigated.
- Sharp contrast between the micro-phases present at ambient conditions.
- Micro-phase formation is liquid–liquid phase separation coupled with a phase change.

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ABSTRACT

Bitumen and bituminous binders are a mixture of a wide variety of molecules with different size and nature; a-polar as well as polar, aromatic as well as aliphatic, chain-like as well as two-dimensional in nature. However, most of the bitumina display at ambient temperatures a spontaneous formation of micro-phases displaying different mechanical properties such as stiffness or adhesive behaviour. The actual chemical composition of the individual phases is still a matter/subject of discussion.

The application of different scanning probe microscopy modes such as FFM, SThM and SNOM enabled the investigation of the relationships between asphalt microstructure and material characteristics such as friction coefficient, thermal conductivity and chemical composition and polarity. It was possible to collect data providing more and detailed information's on a nano-scale and in detail with respect to the different micro-phases present in bituminous binders. All data collected fit into the present picture of structuring of bitumen and the characteristics of the present phases.

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1. Introduction

The fact, that bitumen is more than just a brownish-black sticky substance, but displays a rather surprising rich micro structure is not really new; the spontaneous formation of distinct (colloidal) structures within bitumen is already at least since 1923 under exploration [1]. Such structuring in bitumen is a consequence of the chemical nature. Bitumen and bituminous binders comprise a wide variety of molecules with different size and nature; a-polar as well as polar, aromatic as well as aliphatic, chain-like as well as two-dimensional in nature. Bitumen contains ca. 95% non-polar carbon compounds consisting of a combination of chains and rings,

partially saturated with hydrogen atoms [2] as manifested by an abundance of non-polar hydrocarbon groups, e.g. methyl groups ($-\text{CH}_3$). A portion of bitumen molecules contains also typically one or more heteroatoms – sulphur, nitrogen and oxygen – typically in much smaller quantities (about 5%). The most common naturally occurring functional groups in bitumen are sulfoxide ($-\text{S}=\text{O}$), carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$) and carbonyl ($-\text{C}=\text{O}$) as well as hetero-ring-systems like thiophenes and pyridines. The variation in chemistry at a molecular level results in different intermolecular associations (through hydrogen, ionic, polar or van-der-Waals bonds) and consequently in structuring. The early ideas about structuring resulted in a micellar model developed by researchers of the Bataafsche Petroleum Maatschappij [3], a model picture used for a very long time. In this model, the bulk of such a micelle consists of substances with the greatest

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molecular weight and with a pronounced aromatic nature (asphaltenes), surrounded by lighter constituents of less aromatic nature (resins) and dispersed in heavy, purely viscous oils (saturates).

However, also other effects such as crystallizations of parts of the mixture of compounds within bitumen cause structuring. Phases within bitumen have been identified in the past using thermal microscopy, differential scanning calorimetry [4,5] and more recently atomic force microscopy (AFM) [6–14]. In a number of these experiments, crystallization and melting/dissolution of fractions (phases) in bitumen as a function of temperature was observed; upon heating, a gradual disappearance of the organized domains occurred implying a melting/dissolution of crystals into a liquid-like matrix resulting finally in a homogeneous liquid [8–11]. Upon cooling, there was a gradual precipitation/crystallization into easily identifiable regions of molecular association. The phenomenon is completely reversible when the samples were subjected to numerous heating/cooling cycles. However, at 25 °C, bitumen needed almost 24 h to fully regain structural equilibrium.

Detailed structural studies by AFM enabled the discrimination between two phases in bitumen samples displaying different mechanical properties such as stiffness or adhesive behaviour [15–18].

The actual chemical composition of the individual phases is still a matter/subject of discussion. The early AFM work on bitumen attributed the bee-like structure to asphaltenes [6–8], however, the bee phase can also be related to the paraffin crystallization on the asphalt binder [10–13]. Asphaltenes show an affinity to aliphatic species such as waxes and may act as nucleation sites for crystallization and aggregation of those species as reported earlier as well [19,20]. Consequently, microcrystalline waxes can co-precipitate and crystallize with asphaltenes and result in a highly insoluble, solid-like structure within the bitumen.

Besides the observation of crystallization and the assignment of parts of the bitumen to that by solvent fractionation and testing the impact of removal of different parts to the development of the micro-structures within bitumen, there has been only limited work on identifying chemical composition to the microstructural domains within bitumen. Peterson [21] used differential infrared spectroscopy to identify the relative percentages of various chemical functionalities present in asphalt with respect to the Micellar Model fractions, SARA. The study revealed that the majority of the highly polar constituents of the model (asphaltenes and resins) contain the most polar functional groups, such as COOH and S=O. Trace amounts of the functional groups were also identified in the less polar, naphthene aromatics fraction, while no functional groups were attributed to the saturates fraction of the model. However, the distribution of components of the SARA fraction within the micro-domains is almost unknown.

An interesting experiment was recently performed by Allen et al. [18] while using Chemical Force Microscopy (CFM), to reveal more chemical information with respect to their distribution in the phases of bitumen [22]. CFM is a variation of AFM and uses chemical interactions between a functionalized probe tip and a sample and enables as such the ability to determine the chemical nature of surfaces, irrespective of their specific morphology. Allen et al. investigated the impact of asphalt chemical composition on the microstructure and performance characteristics of asphalt binder while comparing the results obtained using a neutral silicon nitride (Si_3N_4) tip, and apolar $-\text{CH}_3$ functionalised tips and polar $-\text{COOH}$ functionalised tips. This study conclusively shows that in cases where the saturates (oily) fraction of the asphalt is maximised, 'bee' structuring and overall chemical polarity of the asphalt microstructure is significantly higher. Conversely, in cases where the saturates fraction is low, i.e. <13%, 'bee' structuring and overall chemical polarity are much lower at the surface. Chemical SARA

fractions other than saturates seemed to have a minimal and inconsistent impact on the structuring that occurred.

So far, a quantification of the origin of the contrast observable between the phases is limited. Therefore, different modes of the Scanning Probe Microscopy such as friction force microscopy, scanning thermal microscopy and scattering near-field microscope are employed to gain more detailed information about the relation of chemical composition to asphalt microstructure.

The goal of this study is it to establish relationships between asphalt microstructure and material characteristics such as friction coefficient, thermal conductivity and chemical composition and polarity. It will be shown that a surprisingly sharp contrast with respect to the friction properties, the thermal conductivity and the chemical composition between the two micro-phases exist. All methods employed deliver new informations concerning detailed properties of the micro-phases within bitumen on a nano-scale and their origin.

2. Materials and methods

2.1. Material

The bituminous binder used in this study is labelled as Q8 70–100 and was supplied from Kuwait Petroleum Research & Development (Rotterdam, Netherlands) and was derived from Kuwait Crude Export. The penetration (PEN) value was 82, the softening point 45.8 °C and the Fraass breaking point –15 °C. The content of SARA fractions is as follows: Saturates: 3.8%, Aromatics: 59.6%, Resins: 22.2%, Asphaltenes: 14.6%. The determination of the amount of fractions was performed using a Iatroscan apparatus, a combination of thin layer chromatography and FID detection. The separation of bitumen into its four main (generic) components has been done according to their solubility in different solvents (tetrahydrofurane, n-heptane, toluene/n-heptane (80:20) and dichlormethane/methanol (95:5)).

2.2. Preparation of the samples (films)

Bitumen films were prepared by the application of a bead of bitumen onto a silicon wafer, followed by heating for 1–2 min in an oven at about 115 °C to ensure a low viscosity of the binder. Subsequently, thin films (thickness ca. 0.4–2 μm) were prepared using a doctor-blade while still being at elevated temperatures. The sample was cooled down to room temperature which resulted in a smooth and glossy finish of the bitumen film. The sample was subsequently covered to prevent contamination by dust. Prior to imaging, the sample was annealed at room temperature for at least for 24 h.

2.3. Scanning probe microscopy

The friction force microscope (FFM) as applied in this study is a derivative of the atomic force microscope (AFM), which is optimized to measure the lateral forces present between a sharp, nanoscopic tip and a surface during scanning of the tip. A friction force acting on the tip yields torsion of the cantilever which can be recorded as a read out of the left–right signal on the AFM photodiode detector. The top–bottom signal of the sectioned photodiode detector registers the bending which is translated to the topology signal. FFM images were recorded using a Topmetrix Explorer AFM operated in contact mode (probes DNP, cantilever C, spring constant 0.12 N/m) combined with a Linkam heating/cooling stage TP 94. This instrument was as well equipped with the scanning thermal microscopy (SThM) option (Micro-Thermal analyzer, μ -TA 2990, TA Instruments).

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