The microstructure of petroleum vacuum residue films for bituminous concrete: a microscopy approach

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Summary
Selected carbon-rich refinery residues ('binders') mixed with mineral particles can form composite materials ('bituminous concrete') with bulk mechanical properties comparable to those of cement concrete. The microstructural mechanism underlying the remarkable composite properties has been related to the appearance of a rigid percolating network consisting of asphaltenes and mineral particles [Wilbrink M. et al. (2005) Rigidity percolation in dispersions with a structured visco-elastic matrix. Phys. Rev. E71, 031402]. In this paper, we explore the microstructure of thin binder films of varying thickness with a number of microscopic characterization techniques, and attempt to relate the observed microstructure to the distinctive mechanical behaviour. Two binders, only one of which has been proven to be suitable for bituminous concrete were investigated, and their microstructure compared. Both binders show the formation of asphaltene aggregates. The binder suitable for bituminous concrete is distinguished by the fact that the asphaltenes show a stronger tendency towards such aggregation, due to a higher concentration and less stabilization in the maltene phase. They also show a clear affinity to other species (such as waxes) and may act as nucleation sites for crystals and aggregates of those species.

Introduction
Composites consisting of petroleum vacuum residues (VRs), or binders, mixed with mineral particles (MPs), are commonly used in paving applications. These composites typically show ductile behaviour and creep when submitted to prolonged loading, reflecting the viscoelastic nature of the VR. However, selected heavy grade VRs after appropriate heat treatment can produce composites, Bituminous concrete, of which some bulk mechanical properties, for example, the flexural strength in three-point bending are measured around 4–9 MPa in standardized tests NEN 7000 (Nederlands Normalisatie Istituut, 2nd edition, July, 1985), that is comparable to those of cement concrete (Shell patent, 2000; www.c-fix.com). Such VR binder has been made commercially available as ‘C-fix carbon concrete binder’ (Blanken & Mooiweer, 2002; Decleer, 2003).

Vacuum residue (VR) chemistry
VRs are complex mixtures of heterogeneous species differing in molar mass, aliphatic/aromatic nature and polarity. The mixture is traditionally split in four successive solubility classes, with increasing molecular weight and polarity: (free) saturates, aromatics, resins and asphaltenes (Corbett, 1969; note that Corbett did not use the words aromatics and resins, but naphthene aromatics and polar aromatics, however the former are currently most-accepted denominations). Asphaltenes are commonly defined as the crude-oil fraction that is soluble in aromatic solvents (e.g. in toluene or benzene) but insoluble in aliphatic solvents (e.g. in n-heptane – C7-asphaltene or in n-pentane – C5-asphaltene). They are typically large polycyclic–aromatic unit sheets containing hetero-atoms, dipoles and short aliphatic sidegroups; as the heaviest component in the residue they have a strong tendency to aggregate and precipitate out from an initially stable mixture under less favourable conditions. (For overviews of the general aspects of asphaltenes, in particular in relation to bituminous residues, their microstructures and mechanical properties, see Yen & Chilingarian, 1994; Loeber et al., 1998; 2000; Masson et al., 2007; Lesueur, 2009). The remaining solute, including saturates, aromatics and resins fractions, is commonly designated as maltene, whereas the
toluene-insoluble part is referred to as coke. Note that these definitions are strictly operational ways to separate the essentially continuum–polydisperse mixture into characteristic finite fractions, and in particular rely on the solubilities being dependent mainly on dispersive interactions and less so on polarity.

A generally accepted concept of VR is that of a colloidal suspension of asphaltenes in a maltene phase (Pfeiffer & Saal, 1940). Asphaltenes can be peptized by the resin fraction, which represents the heaviest, most polar and aromatic compounds of the maltene phase. Different VRs may be compared using a colloidal index, CI (Loeber, 1998):

\[
CI = \frac{\text{aromatics} + \text{resins}}{\text{saturates} + \text{asphaltenes}},
\]

A higher CI means that asphaltenes are more peptized by the resins from the viscous maltene. For a sufficiently high CI, the asphaltenes may be fully peptized and move through the maltene only limited by the viscosity; the VR is then of the sol-type. Gel-type VR occurs if partially peptized asphaltenes aggregates across several length scales, inducing a percolating network of finite elasticity. According to Lesueur (2009), the existence of a gel structure in VR is not substantiated by any rheological evidence as no yield stress or modulus plateau was ever observed on VR. However, if the percolation effect perhaps does not occur in bulk, it was observed over smaller length scales (Wilbrink, 2005).

The molecular picture of asphaltene peptization is that the resins attach to the asphaltenes with their aromatic and polar groups and stretch their aliphatic groups outwards to form a steric stabilisation layer around the asphaltenes.

**Mechanical behaviour**

As was indicated earlier, mixing of selected VR with MPs followed by thermal hardening yields a composite material with extremely favourable mechanical properties. Understanding the macroscopic mechanical behaviour of bituminous concrete in terms of its microstructure was first attempted by Wilbrink et al. (2005). They postulated that the asphaltene fraction in the VR creates mechanical bridges between the MPs that are subsequently strengthened in the high-temperature treatment of the mixture. To test the bridging hypothesis, they used simple model mixtures consisting of mono- or bi-modal distributions of spherical mineral particles dispersed in the binder. The mechanical properties of the mixtures were determined in a rheometer. Changing the size, dispersion or volume fraction of the MP, and thereby the characteristic size of the ‘pore’ space between the MPs, was found to have a direct impact on the mixture mechanical behaviour. Clear evidence for the occurrence of a threshold for rigidity percolation was obtained. Percolation apparently only took place if the average ‘pore’ size was below a critical size of about 600 nm. It was assumed that at this scale asphaltene aggregates in the binder could indeed bridge the pores, effectively creating a percolating network together with the MPs, thus providing rigidity to the composite. This gel-type rigidity is subsequently orders of magnitude enhanced by high-temperature treatment.

The microscopic hypothesis underlying the explanation of the percolation behaviour has not been confirmed so far by direct observation, and *in situ* investigation using microscopy is called for. Therefore, this paper focuses on microscopy of VR for bituminous concrete. Bearing in mind the results of Wilbrink et al. (2005), and particularly the occurrence of a characteristic length scale determined by the characteristic size of asphaltene aggregates, spin-coated thin-films of varying thickness are investigated, serving as an analogue for interparticle films in composites with the advantage of offering an open surface for characterization using several microscopic techniques.

By the nature of the chosen atomic force microscope (AFM) method (also proven valuable in studies by others), different boundary conditions have to be accepted. However, the spin-coating leads to a deep and rapid quench for the insoluble components such as asphaltenes and wax, which already have a natural tendency to phase separate in the bulk and need no nucleation surface. So the effects of the different boundaries are expected to be minor, and not too different between different samples. Of course in the interpretation it has to be realized that samples are probed from the top surface only.

The correspondence between the characteristic length scales for asphaltene-aggregate confinement in composite and spin-coated thin-film configuration is depicted in Fig. 1.

The paper is structured as follows. The materials and experimental techniques used are described in the next (second) section. In a third section, the microstructure of spin-coated thin films is presented and discussed for two types of binders and for different film thicknesses. As one of the binders did not show rigidity percolation in model composites whereas the other did, differences in aggregation behaviour of the asphaltene fraction are anticipated. The microstructures are then compared to similar films spin-coated from ‘pure’ asphaltene and ‘pure’ maltene. Moreover, the structure of films recombined from varying proportions of the ‘pure’ asphaltene and ‘pure’ maltene are shown. The effect of annealing on the observed microstructures is investigated. The discussion converges in an overall interpretation, after which conclusions are summarized in the final section.

**Materials and methods**

**VR binders**

Two VR binders are considered, designated as B1 and B2. Only B1 proved suitable for producing good ‘bituminous concrete’ composites. The binders are refinery residues from deep thermal conversion processes, but differ in crude-oil
Fig. 1. Asphaltene-aggregate confinement in composite (left) versus thin film (right) configuration – d, MP diameter; \( \Lambda \), characteristic length scale; \( \phi \), MP volume fraction; \( \phi_{\text{max}} \), maximum MP fraction (0.64 for a random distribution of mono-disperse spheres).

origin and cracking severity. Sample B1 originates from a high-sulphur Middle East crude, whereas sample B2 originates from a low-sulphur European crude. B1 and B2 have densities \( \rho \) equal to 1.094 and 1.047 g cm\(^{-3} \), and contain 24.9\% and 13.2\% (w/w) C\(_7\)-asphaltenes, respectively; B1 is not only richer in asphaltenes, but has a disproportionally larger amount of hetero-atoms (S, V, Ni); also the size of the aromatic sheets is different: NMR analysis indicates that in B1 the number of aromatic rings per unit sheet is 17.6 and 4.3 for the asphaltenes and maltenes, respectively; for B2 these numbers are 13.6 and 3.5, respectively (all data from private communication, Shell Global Solutions). B1 and B2 are raw residues from refinery processes and did not undergo any heat treatment such as the thermal hardening used to yield a final composite material from a VR with MPs mixed in.

Fractionation of binders into asphaltene and maltenes components

Five grams of binder was dissolved in 200 mL of \( n \)-heptane. The solution was kept in an oil bath at 80\^\circ \) C for 2 h. The solution was then filtered using two superposed paper filters. A heptane-insoluble fine brown powder remained on the filter paper. Heated \( n \)-heptane was further poured on the brown powder to dissolve any remaining C\(_7\)-soluble fraction, until the drained solvent would become colourless. The brown powder was kept in sealed plastic bag for further analysis; the C\(_7\)-soluble fraction was left uncovered under a fume hood, until all solvent had evaporated. All material obtained was used within 1 month.

The above procedure to separate the two ‘components’ in the essentially polydisperse mixture constitutes our own operational definition of ‘asphaltenes’ and ‘maltenes’. In particular, the solution time of 2 h was chosen to minimize oxidation. Standard practical and industrial procedures may differ in this respect (see, e.g. Speight, 2004) – in particular the separation process used by Shell to quantify the weight concentration of C\(_7\)-asphaltene reported in the previous paragraph – but are equally operational; the main purpose of our procedure was the same: to define in a consistent manner qualitatively different heptane-insoluble and heptane-soluble components, which henceforth will just be termed (C\(_7\)-) asphaltenes and (C\(_7\)-) maltenes, respectively. In view of all operational aspects conclusions regarding the behaviour of the components will largely be qualitative as well.

Thin-film preparation

Thin films were prepared by spin-coating, for each binder, for reconstituted binders based on the fractionated components, and for the separated asphaltenes and maltenes. Solutions were prepared by dissolving a (fractionated) binder in toluene at different concentrations: 2, 5, 20 and 50\% (w/w). The solution was filtered, using first a coarse, then a fine (0.2 mm pore size) filter. Glass slides, cleaned in an ultrasonic bath of soap and water followed by distilled water and ethanol, were used as substrate. The binder solution was spread on the glass slide and rotated at constant speed ranging from 500 to 5000 r.p.m. for 120 s, with an initial acceleration of 2000 r.p.m. s\(^{-1} \). 1 r.p.m. corresponds here to 0.1 g. Film thickness (averaged depth of a series of scalpel scratches) ranged from 40 nm to 10 \( \mu \)m for B1 and 120 nm to 8 \( \mu \)m for B2.

From now on, binder thin films will be referred to along the text using the following notation: Bn-T\%RPM, where Bn stands for B1 or B2, T\% for the concentration in toluene (2–50\%) and RPM, the spin-coating speed (500–5000 r.p.m.).

Microscopy

A Zeiss Axioplan 2 reflection optical microscope was used in bright field. Images were acquired with a colour digital camera, and subsequently numerically divided in red, green and blue channels; the channel showing maximum contrast was selected to produce a greyscale image.

A Digital Instruments Dimension 3100 AFM was used in tapping mode. Topography and phase-contrast images were measured simultaneously. Image processing was limited to first-order flattening, which consists of subtracting a line from each scan line to optimize contrast.

For transmission electron microscopy (TEM) observation, thin films were carefully peeled off from their supporting glass
slides via flotation at the surface of distilled water. The floated thin film was collected on a TEM grid, excess water being removed by means of a filter paper applied edge-to-edge to the grid. A JEOL2000 TEM operated at 80 kV was used for observation in bright field and diffraction mode.

Results

Thin-film microstructure overview

To set the stage, a number of typical observations of B1–5%4000 with different imaging techniques are presented in Fig. 2. The film thickness (averaged depth of a series of scalpel scratches) was measured by AFM to be around 100 nm.

‘Flower’-like domains are imaged by all four imaging techniques, with a characteristic lateral size of about 10 µm. Features a few micrometre in size (dark on TEM image, light/protruding on AFM height image) are present at the edges of the ‘flower-like’ domain. These deposits are presumed to generate distinctive hexagonal diffraction patterns in TEM (see selected-area electron diffraction pattern in Fig. 2b); the patterns disappeared quickly in the beam and it was difficult to locate the diffracting element in real space. Higher magnification AFM images for B1–5%2000 are presented in Fig. 3. At the highest magnification (Figs 3c and d), the ‘flower-like’ domains appear to be porous (pores less than 100 nm in size) and surrounded by a substance where scanning artefacts may result from tip-surface intermittent adhesion.

Thin films with increasing thickness

AFM tapping-mode phase images of a series of films spin-coated at different rotation speeds (500–5000 r.p.m.) from solutions with different concentrations (2–50%, w/w) are shown in Figs 4 and 5 (B1), and Fig. 6 (B2). The corresponding film thickness estimated via AFM and nano-indentation (Tamminga et al., in preparation) is indicated. Thickness clearly increases with concentration and decreasing rotation speed. Spin-coated film thickness is stated by some authors to be proportional to $f^{-\lambda}$, where $f$ is the spin speed in r.p.m. and $\lambda$ lies between 2/3 and 1/2 (Meyerhofer, 1978; Lawrence, 1990). Thus, films formed at 1000 r.p.m. should be about twice as thick as films formed at 3000 r.p.m., which is in reasonable agreement with our measurements.

As illustrated in Figs 4–6, with increasing film thickness the ‘flower-like’ domain area initially increases until it covers...
Fig. 3. AFM of B1–5%2000: (a) and (c) topography, (b) and (d) phase. The bottom-row images cover the black square drawn on the top-row image. Asphaltene appears as aggregates embedded in another (presumably maltene) phase. Small protruding domains have nucleated on the edges, and are believed to be wax crystals. Note the difference in surfaces texture between the two types of aggregates, ‘porous’ for the asphaltenes, smooth for the wax crystals.

up the entire film surface (film thickness ranges then from 3 to 4 µm). As the film thickness further increases, the visible (emerging) fraction of domains becomes smaller for B1 films. Simultaneously, outgrowths are observed at the surface. They appear to nucleate from edges and (for increasing thickness and hence also slower evaporation) increase in area and (stepwise) in height. The steps are most likely associated with a spiral growth, and indicate crystalline ordering. Eventually they cover almost the entire domain.

Domain aggregates in B2 show a similar surface and local edge structure as those in B1, indicating a similar physical growth process. However, in contrast to B1, the aggregates observed on B2 films do not show a flower-like shape.

Microstructure of the asphaltene fraction
AFM tapping-mode images of C\textsubscript{7}-asphaltene films are shown in Fig. 7. The asphaltene networks are essentially identical, although they differ slightly in characteristic size: 50–100 and 10–50 nm for B1 and B2, respectively. Decreasing the setpoint, that is tapping harder on the surface, allows penetrating a ‘coating’ overlaying the asphaltene network on the phase-contrast image; this effect is only observed for the B1 C\textsubscript{7} asphaltene fraction.

The spin-coated films in Fig. 7 (samples A1 and A2) have been prepared with equal starting concentrations in toluene of the separated asphaltenes. Nevertheless, there is a slight difference in the characteristic network structure of the precipitated asphaltenes, the sample A1 giving a somewhat higher porosity.

Microstructure of the maltene fraction
AFM tapping-mode images of C\textsubscript{7}-maltene films are shown in Figs 8 and 9. Interestingly, domains appear on these films similarly those observed on the thin (<150 nm) VR films (Figs 4 and 6). On the thickest B1 C\textsubscript{7}-maltene films, lozenge-shaped crystals (Fig. 8, 50% 500 r.p.m.) form.
Structural changes upon annealing

The effect of annealing on the structure of B1 and B2 binder thin films was investigated. To that end B1–5%5000, B1–50%5000, B2–5%5000 and B2–50%5000 were submitted to temperature–time trajectories as depicted in Figs 10 and 11. Thin films on glass substrate were heated at a rate of 20°C min⁻¹ up to 60°C in stage I and to 120°C in stage II, and kept at these respective temperatures for 2 min. After each stage, the samples were cooled down to room temperature (RT = 25°C), assumed to be reached within 15–30 min, and then observed by AFM. Unstable VRs may take a very long time to equilibrate, if at all, in particular with respect to the heaviest components. More important is therefore a uniform procedure from sample to sample.

On B1–5%5000 (Fig. 10), after stage I, domains showed a tendency to string together by further aggregation. After stage II, strings were broken, releasing scattered isolated, fairly mono-dispersed domains (similar to those observed on B2 films).

On B1–50%5000, after stage I, the large aggregates broke down into isolated domains. Simultaneously, crystals grew in size, still located at the aggregate edges. After stage II, the aggregates decreased in area and strung together.

On B2–5%5000, domains increased in size after stage I, with formation of a shell around the core domain (Fig. 11). This shell shows both on topography and phase contrast. After stage II flower-like aggregates formed, resembling those found on freshly spin-coated B1.
On B2–50%5000, the effect of elevated temperature on domain size is again significant. Domains initially \( \sim 1 \) µm in size, grew to a few µm following stage I, and reached up to 15 µm following stage II. Remarkably, the domain structure became also increasingly distinct, with the formation of ‘bee’-like wavy fringes at the domain centre.

Microstructure of recombined binders

To investigate to what degree the asphaltene content influences the binder microstructure and aggregation properties, B1 and B2 were recombined from their fractionated C\(_7\)-asphaltene\(\text{Bn}\) and C\(_7\)-maltene\(\text{Bn}\), to match the asphaltene...
mimic true residues of the corresponding composition. Following such a procedure, the components were dissolved and mixed in toluene before spin-coating. The initial C₇-asphaltene concentrations for B1 and B2 (25% and 12%, w/w), were thus brought to 12% and 25% (w/w), respectively. Microstructures of these recombined materials are shown in Fig. 12. Clearly, the binders with the same asphaltene content show very similar microstructures. However, possibly significant differences do exist. In the recombined B1 the aggregates are markedly polydisperse, and do not show a similar increase in aggregate density as the film becomes thicker. In recombined B2, aggregates are comparable in size and shape to the ones formed in B1. However, in recombined B2 domains clusters differ in being somewhat more compact and showing no sign of crystallite nucleation at its surface.

Discussion

Thin-film microstructure overview

The ‘Flower-like’ domains imaged in Fig. 2 by four imaging techniques and with a characteristic lateral size of about 10 µm are attributed to asphaltene aggregates. Indeed asphaltenes generally represent the first component to separate out from a residue under toluene evaporation, and their shapes are consistent with rapid aggregation under a strong (concentration) gradient (‘Laplacian growth’, see, e.g. Barra et al., 2001); flower-like diffusion-limited aggregation (DLA)-type aggregates of asphaltenes comparable in shape and size were already observed with AFM by Toulhoat et al. (1994); these aggregates formed at the surface of cleaved mica sheets dipped for a preset time (comparable to the time we used for spin-coating, i.e. 120 s) in a solution of asphaltenes in toluene. Apparently the domains reflect less light (are darker in optical microscopy), and scatter less electrons (lighter in bright-field TEM). To some extent this may result from thickness differences, but the tapping-mode phase image clearly indicates that the flower-like aggregates and surrounding material are different. Other published AFM investigations show DLA-type asphaltene aggregation similar to what we observed. Ese et al. (2000) report AFM examination of the topography of monolayers of asphaltenes and resins transferred by Langmuir–Blodgett

Fig. 7. AFM tapping-mode images. C₇asphalteneB1–5%5000 (top) and C₇asphalteneB2–5%5000 (middle and bottom) – columns (a) topography and (b) phase contrast. Bottom row illustrates the influence of decreasing the tapping-amplitude setpoint, equivalent to moving the tip towards the specimen surface.

concentration of their counterpart. As with the fractionation, the recombination procedure has to be defined in a practical manner which is kept the same throughout the experimental investigation; the process by which the original binders were formed cannot be reproduced at the laboratory timescale, and the resulting reconstituted binders will at best qualitatively

Fig. 8. AFM tapping-mode phase images: C₇malteneB1–5%5000, C₇malteneB1–5%500, C₇malteneB1–50%5000 and C₇malteneB1–50%500.
Fig. 9. AFM tapping-mode phase images: C7malteneB2–5%5000, C7malteneB2–5%500, C7malteneB2–50%5000 and C7malteneB2–50%500.

Fig. 10. AFM tapping-mode images of B1–5%5000 and B1–50%5000 submitted to annealing as depicted on top.
deposition technique from water to mica substrates. They see a heterogeneous nucleation process giving growth of fractal asphaltene aggregates resembling those observed by Toulhoat. As the resin fraction increases the close-packed structure of irregular-shaped asphaltene domains 'opens' leading to formation of a smoother domain pattern. Zhang et al. (2005) examined adsorbed monolayers of fractionated high molecular weight asphaltenes at an interface of water and a heptane/toluene mixture, transferred onto hydrophilic silicon wafers by a Langmuir–Blodgett deposition method. Contact mode AFM topographic images of the monolayer Langmuir–Blodgett films show asphaltene colloidal particles formed from molecular asphaltene. At the highest heptane concentrations, the precipitated asphaltenes form irregular DLA-like aggregates and networks.

The domains reported in our work show two distinct 'textures' and phase contrasts (AFM); one texture is porous with clear phase contrast (Figs 3 and 6) which resembles isolated C7-asphaltene (Fig. 7), another texture is stepwise and smooth with dark phase contrast. The size of the dark-phase
features is in fact growing in size and gradually covering up the clear-phase domains as the film becomes thicker (up to 10 µm in lateral size on 10 µm thick films in Fig. 4). These dark-phase and stepwise smooth features likely correspond to the domains reported in Lu et al. (2005). The dark-phase contrast suggests a material softer than the asphaltenes or resins (Masson et al., 2006) and is very likely wax – the embedding phase is even darker due to the viscosity of the saturates. Therefore, we believe that in spite of the difference in considered dimensions (Lu et al. consider film thickness in the mm range) and used resolution (Lu et al. mostly use light microscopy, so much lower resolution), our observations corroborate those of Lu et al., yet addressing uncertainties about the distinction wax–asphaltene that still remained in their publication.

The porosity of aggregates seen on higher magnification AFM images for B1–5%2000 (Fig. 3) is also reported by Espinat et al. (1998), Pérez-Hernández et al. (2003) and Loeber et al. (1996) for asphaltenes. The substance that generates scanning artefacts from intermittent tip-surface adhesion is most likely the viscous phase surrounding domains (Lord & Buckley, 2002).

SAED patterns in Fig. 2 are from a single crystal isolated over at least a 1-µm-wide area (effective diameter of the SA aperture at the plane where image area is selected); the small ‘precipitates’ visible at the edge of the domains are ranging in size between 300 and 500 nm in Fig. 3(d). The SAED patterns are identical to the 0 k l electron-diffraction pattern reported for epitaxially grown n-alkane wax samples (blend of n-paraffin from n-C26 to n-C30) (Srivastava et al., 1993) but also for plant epicuticular waxes (Ensikat et al., 2006), with a morphology (stepwise platelets) and size (few hundred nanometres to 1 µm) in good agreement with our observations. Even assuming that the porous flower-like pattern would have an underlying crystallinity, we would expect a ring-shaped diffraction pattern (similar to Debye-Scherrer powder patterns) to form from a 1-µm selected area. It is therefore assumed that wax crystals have nucleated on the edges of the aggregates. This is supported by the notion that a minor fraction of heavy wax is present in the residue (in the binder B1, ca. 0.5% – data provided by Shell Global Solutions), and that during toluene evaporation this heavy component will separate out of the receding toluene/maltene phase (vide infra).

In summary, our interpretation is therefore that the flower-like patterns visible on films a few hundred nanometres thick correspond to DLA-type asphaltene aggregates peptized by the resins and aromatics, and covered with wax crystallites.

**Thin films with increasing thickness**

As illustrated in Figs 4–6, the asphaltene aggregate area increases with increasing film thickness until it covers up the entire film surface (film thickness ~3–4 µm); then the visible (emerging) fraction of asphaltene domains becomes smaller for B1 films as the film thickness further increases. Simultaneously, outgrowths observed on the surface appear to nucleate from edges and (for increasing thickness and hence also slower evaporation) increase in area and (stepwise) in height, most likely associated with spiral-grown crystals. Eventually, they cover almost the entire domain. Paraffin waxes may again be the crystallizing species (Wiehe & Liang, 1996; Plomp et al., 2000; Kané et al., 2003). Saturates may migrate from the surrounding oil to condensate on asphaltene domains, and will have more time to do so for slower solvent evaporation. Indeed, wax is known to nucleate at aliphatic side-chains and then grow on top of high-surface-energy asphaltene domains (McLean et al., 1998).
Asphaltene aggregates in B2 show a similar surface and local edge structure as those in B1, indicating a similar physical growth process, but do not show a flower-like shape. This is consistent with aggregation with a lower sticking probability as would be expected for a smaller difference in aromaticity and polarity between more fully peptized asphaltenes and maltenes in B2.

Using the NMR data and molecular modelling, Murgich & Abanero (private communication) calculated the difference in cohesive-energy density between asphaltenes and maltenes for the two binders. They found a larger cohesive-energy density difference for B1, concluding that the asphaltene was less ‘miscible’ in the associated maltene, or in other words, that the segregation of the asphaltenes from the associated maltene should be more pronounced than in B2. Puig et al. (2004) used inverse gas chromatography and found a higher dispersive (Van der Waals) surface energy for B1.

The thickness of the films in Figs 4 and 5 (sample B1) is determined by the rotation speed during spin-coating and by the viscosity – that is the binder concentration in the solvent. As this thickness is roughly inversely proportional to the time for solvent evaporation, the order of the frames in Fig. 5 is that of increasing time before structures become fixed. So the first frames of Fig. 5 correspond to a low concentration of asphaltenes and a short time: for asphaltenes with a strong aggregation tendency a flower-like pattern as observed here may then be expected, because it points at precipitate growth under a strong (concentration) gradient (Barra et al., 2001). In accordance with this, for larger times and higher concentrations the pattern weakens, whereas the total amount of precipitated asphaltenes and the asphaltene particle size both increase; also, for longer times the patterns may change through a restructuring of the aggregates. At the highest concentrations (highest viscosities), the effect of rotation speed on film thickness becomes minimal, while the trend in amount and particle size of the precipitate reverses.

One explanation of the latter may be that in this regime the aggregation is more dominated by shear-induced ballistic coagulation, and hence decreases with decreasing rotation speed. A simpler explanation may be that in these thicker films the asphaltene aggregates get covered more by the surrounding maltene medium.

Figure 6 (sample B2) also shows precipitates growing in amount and size with time, but there is no sign of a diffusion-limited Laplacian-growth mechanism. So the asphaltenes do precipitate but seem better solvated in the binder by their resin counterparts than in B1, if only because their concentration is so much lower.

One remark on the phase contrast inversion: the same observation was made by Masson et al. (2006) and interpreted as a possible change in the tip-sample interaction, affected by the sample modulus and the hydrophilic/phobic interactions between the tip and the sample (see also references therein). Masson et al. hypothesize that either steric hardening or the slow oxidation of the bitumen surface in air causes the inversion, still under investigation by the authors at the time of their publication.

Microstructure of the asphaltene fraction

The asphaltene networks observed on A1 and A2 films (Fig. 7), essentially differing only slightly in characteristic size, once again indicate that the ‘porous’ domains pointed out in Figs 2–6 are indeed containing asphaltene. Scanning stability is improved here due to the absence of maltene.

The presence of a ‘coating’ overlaying the B2 C7-asphaltene fraction, as evidenced by decreasing the setpoint, may be related to the more aliphatic nature of the asphaltene. Aliphatic side chains are not involved in asphaltene stacking and may form a soft-textured layer of free-hanging chains.

Microstructure of the maltene fraction

Domains observed on C7-maltene films (Figs 8 and 9) are quite similar in surface texture to the asphaltene domains observed on VR films (Figs 4 and 6). Li et al. (1999) report similar observations, arguing that the n-heptane soluble but n-pentane insoluble fraction could still form domains even if deprived from C7-asphaltenes. This is quite logical in view of the operational definitions of the components, which assume excess amounts of solvent.

On the thickest B1 C7-maltene films the lozenge-shaped crystals (Fig. 8, 50% 500 r.p.m.) are similar to solution-grown crystals of n-alkane. These crystals characterized by regular spiral growth are reported elsewhere in the literature (Chichakli & Jessen, 1967; Srivastava et al., 1993).

In the maltene films of Figs 8 (M1) and 9 (M2), the heptane insolubles are absent, but nevertheless a solid phase precipitates during spin-coating. These are therefore presumably polycyclic structures of lowest molecular weight and heavy resins. The M2 films form larger domains and thicker films under identical spin-coating conditions, suggesting more of such maltene-compatible smaller polycyclics. The domains remain small, so there is no strong tendency to aggregate. More striking is the often anisometric shape of the solid particles. Whether this is related to the anisotropic molecular shape, and to any mesophase intermolecular order and anisotropic interfacial tension (as is the case with so-called ‘tactoids’, see, for example Prinsen & van der Schoot, 2003) remains as yet an open question.

Structural changes upon annealing

In Fig. 10 (original binder B1), it is observed that after a heat treatment till 60°C, the low-concentration sample shows further aggregation of the asphaltenes. Given the already observed strong aggregation tendency of the asphaltenes in low-concentration B1 this may be explained by the temporary
lowering of the viscosity, which facilitates precipitation of thermodynamically unstable components; in addition, the higher temperature may further increase the asphaltene instability in the nonregular mixture, because asphaltenes are not only solvated by dispersion forces, and, for example, hydrogen bonds breakdown at higher temperature. After a second treatment till 120 °C, the tenuous aggregate structure breaks irreversibly, leaving a final phase of dispersed particles with elongated shape. Rastogi (private communication) performed SAXS measurements on B1 and B2 at the ESRF, Grenoble. In particular, he registered the scattering intensity I(q) of B1 around scattering momentum \( q = 0.03 \text{ Å}^{-1} \) versus temperature, heating the samples at a rate of 10 °C min\(^{-1}\). In a first heating-cooling cycle, the intensity initially increased, subsequently collapsed above 120 °C, and remained far below its original room-temperature value in following cycles. Already in the second cycle a stable new picture of log \( I(q) \) versus log \( q \) developed up till the maximum temperature of 170 °C, with a slope around \(-1\) in the narrow range of \( q = 0.02–0.04 \text{ Å}^{-1} \). This indicates a new mesophasic ordering around the 10 nm scale. By contrast, sample B2 showed in this range of \( q \) an intensity maximum at 60 °C, a decrease upon further heating and a restoration of the original room-temperature intensity after cooling.

Our results are in line with the SAXS observations and once more suggest that the asphaltenes in B1 are already metastable at room temperature. Again one may speculate whether the final phase is oriented; such liquid–crystalline mesophases are known to occur when heavy asphaltenes precipitate out of a supersaturated residue (see, e.g. Gentzis & Rahimi, 2003).

At high concentration (50%), the B1 aggregates are already dense, with an ordered phase of probably wax on top. As a result, the first heat treatment shows no further aggregation, rather some breakdown. A very marked breakdown into elongated particles is again visible after the heating till 120 °C. The wax-like pattern remains visible as well.

In Fig. 11 (original binder B2), the heat treatment till 60°C has resulted in larger particles, but without the irregular growth characteristic for rapid DLA. However, the particles are again strikingly anisotropic, with the mentioned core-shell pattern. Whether the core and shell relate to different components (e.g. asphaltene and resin) is an open question, but anyway the shell disappears after further heating till 120 °C and cooling down again. In the final room-temperature image, rapidly aggregated domains of asphaltenes are observed instead. This indicates that above 60 °C some barrier to rapid asphaltene aggregation has been removed, possibly through breakup of stabilizing interactions with resins.

The high-concentration B2 sample has already a fairly compact structure, and the major effect of the heat treatments is the appearance of the unresolved ‘bee’-like features topping domains with size increasing with the temperature. These ‘bee’-like structures on the most compact precipitates have been observed before under similar circumstances (Loeber et al., 1996; Masson et al., 2006), and are termed a ‘catana phase’, but their origin is still under debate (Lesueur, 2009). They are hypothetically related to a high asphaltene content or to the metal content. One may also speculate that these features form due to mechanical constraints upon cooling from high to ambient temperature.

**Microstructure of recombined binders**

The major conclusion from Fig. 12 (recombined B1 and B2) is that samples with equal asphaltene concentration are much alike in their pattern, so concentration plays a dominant role for asphaltene stability and precipitation, and in particular points at a dominant difference between the two original binders. Minor differences between R1 and R2 are harder to interpret, also in view of the limitations of the reconstitution method.

**Summary of the AFM analysis**

The AFM analysis of thin films with different preparation conditions reveals much detail that may distinguish the original binders. Although the method is qualitative, some details fit very well into a thermodynamic picture also based on the mentioned other studies on these samples (see, e.g. SAXS results reported earlier). Other details still leave room for speculation, and motivate deeper investigation by complementary methods.

Clearly, the analysis confirms that asphaltene concentration is the major factor in forming solid aggregates that may give rise to stress-carrying percolating networks in the binder films. Also it is obvious that this tendency is stronger in B1 than in B2. However, in addition to concentration there seems to be an intrinsic factor here, which may well be a stronger asphaltene–maltene mismatch as suggested by the NMR analysis and molecular modelling mentioned in Section ‘Fractionation of binders into asphaltene and maltene components’. The heating experiment suggests that B1 is metastable, and at 120 °C converts irreversibly to a different phase, with a collapse of the initial aggregates; this is well in line with the earlier SAXS observations. No similar behaviour is observed in the original B2. Rather, asphaltene aggregation as in room temperature B1 is only significant in B2 after a heat treatment till 120 °C.

The AFM results very well visualize also the tendency of wax in B1 to crystallize with time on top of the asphaltenes. Whether this plays a role in the mechanics is unclear.

Very interesting is the appearance, at various stages, of anisometric precipitated particles, in particular in the thermally destabilized sample B1. It is worthwhile investigating the microstructure for any mesophasic ordering. If such ordering would be found, as in coke-precursor
mesophase during cracking of residues (Gentzis & Rahimi, 2003), a logical next question would be whether it has any relation with the distinct mechanical behaviour of B1.

**Conclusion**

The microstructure of two VRs (B1 and B2) showing contrasting mechanical behaviour when mixed with mineral particles to form a composite (B1 showing rigidity percolation in certain composites where B2 does not) has been investigated. Thin films, spin-coated from the two full binders as well as from their respective asphaltene and maltene fractions in solution in toluene, have been characterized using optical microscopy, TEM, and tapping mode AFM. Asphalten domains formed from the two different binders showed differences in their growth behaviour, the asphaltene in the good concrete binder showing more, and more irregular, aggregation. This was explained in terms of asphaltene concentration and of asphaltene stability towards the maltene components. In addition, the latter asphaltenes acted as nucleation sites for wax crystallization. The formation of larger aggregates in B1 corroborates the assumption of a percolating stress-carrying network linking filler particles and asphaltene aggregates, and providing rigidity to composites of B1.

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**References**


