MASTER

Microstructure and micromechanics of confined hydrocarbon binders

Tamminga, A.Y.

Award date:
2004

Disclaimer
This document contains a student thesis (bachelor’s or master’s), as authored by a student at Eindhoven University of Technology. Student theses are made available in the TU/e repository upon obtaining the required degree. The grade received is not published on the document as presented in the repository. The required complexity or quality of research of student theses may vary by program, and the required minimum study period may vary in duration.

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain

Link to publication
Microstructure and Micromechanics of Confined Hydrocarbon Binders

A.Y. Tamminga

June 2004

Master’s Thesis

Study performed at the departments of Applied Physics, Mechanical Engineering and Chemical Engineering and Chemistry of the Eindhoven University of Technology.

Supervisors: Dr. E.D. Sourty (Department of Applied Physics, TU/e)
            Prof. dr. M.A.J. Michels (Department of Applied Physics, TU/e)
            Dr. ir. W.P. Vellinga (Department of Mechanical Engineering, TU/e)
Abstract

The focus of this study is to obtain knowledge on the C-fix microstructure in relation to its mechanical properties. It has been shown that C-fix has bulk mechanical properties comparable to those of cement concrete. Recent investigations on C-fix have shown a relationship between the microstructure of the petroleum vacuum residue—used as a C-fix binder—and the rise of a percolating network, providing rigidity to the C-fix.

Atomic force microscopy, nanoindentation and lateral force apparatus have been used to study the microstructure and micromechanics of two petroleum vacuum residue (PVR) binders—with a difference in asphaltene content—in a thin-film confinement.

Both binders, feature asphaltene domains surrounded by a smooth maltene phase observed at the thin-film surface. The asphaltene domains mainly differ in: mutual interaction, presumed adhesion to the substrate and paraffin wax growth. Not only the amount, but also the reactivity of the asphaltene aggregates, contributes to these differences.

The hardness and elastic modulus of the two binders appear to depend on the asphaltene content, as one binder appears to be in transition between maltene and asphaltene, whereas the other behalves almost like maltene. However, the asphaltene content does not sufficiently account for both qualitative and quantitative differences in mechanical properties between the two binders.

Lateral force measurements shows that one binder has a solid-like behaviour, whereas the other shows viscous behaviour. The difference in asphaltene content contributes to this opposite behaviour.
Table of Contents

Abstract

Table of Contents

Chapter 1 Introduction

1.1 Environmental aspects of C-fix 2
1.2 Constituents of PVR binders 2
1.3 Asphaltenes association 3
1.4 Previous work 4
1.5 Present study 5
1.6 General overview of project 6

Chapter 2 Materials and Methods

2.1 Sample preparation 7
2.1.1 Binders 7
2.1.2 Fractionation 7
2.1.3 Spin-coating 8
2.1.4 Melted binders 10
2.2 Atomic Force Microscopy 11
2.2.1 Introduction 11
2.2.2 Set-up 11
2.2.3 Tip-sample interaction 12
2.2.4 Tapping mode 13
2.3 Nanoindentation 14
2.3.1 Introduction 14
2.3.2 The nanoindenter 14
2.3.3 The Oliver-Pharr method 17
2.3.4 Issues related to nanoindentation 20
2.3.4.1 Substrate effect 20
Chapter 3  Atomic Force Microscopy

3.1  Introduction 25
3.2  Different binders 25
3.3  Asphaltene 28
3.4  Maltene 29
3.5  Asphaltene and maltene 30
3.6  Discussion of results on different binders 30
3.7  Hotstage 32
3.8  Melted binders 36
3.9  Conclusions 37

Chapter 4  Nanoindentation

4.1  Introduction 38
4.2  Hardness and elastic modulus 38
4.3  Influence substrate on mechanical properties 41
4.4  Elastic modulus and hardness: interaction film and substrate 41
4.5  Effect of pile-up 42
4.6  Effect of surface: indentation size effect 43
4.7  Mechanical properties of binders 44
4.8  Comparison between mechanical properties of thin-films from spin-coated and melted binders 45
4.9  Influence of asphaltene content on mechanical properties 45
4.10  Comparison of the elastic modulus of thin-films and storage shear modulus of bulk composite 47
4.11  Conclusions 48
<table>
<thead>
<tr>
<th>Chapter 5</th>
<th>Lateral Force Apparatus</th>
<th>49</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>49</td>
</tr>
<tr>
<td>5.2</td>
<td>Microscopy of scratches</td>
<td>49</td>
</tr>
<tr>
<td>5.3</td>
<td>Mechanical properties of scratches</td>
<td>51</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusions</td>
<td>53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 6</th>
<th>General Conclusions</th>
<th>54</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Microstructure</td>
<td>54</td>
</tr>
<tr>
<td>6.2</td>
<td>Micromechanics</td>
<td>54</td>
</tr>
</tbody>
</table>

References 56

Key to Symbols 59

Acknowledgements 60
Chapter 1

Introduction

A crude oil consists of a mixture of hydrocarbons that can be separated into refinable fractions by distillation. The residual material after distillation is called petroleum vacuum residue (PVR). PVR hydrocarbons are widely used as binders in pavements because of their good adhesion to mineral aggregates and viscoelastic properties. They are also used in water-resistant materials like industrial floors, sewer pipes and dyke elements [1, 2], c.f. figure 1.1.

Figure 1.1: Some applications were PVR hydrocarbons are used as a C-fix binder. From left to right: dyke element, modular road construction, sewer pipe and breakwater block [3].

Due to their viscoelastic nature, PVR binders typically show ductile behaviour and a tendency to creep. However, selected —very heavy, carbon-rich— binders mixed with mineral particles can produce composites with bulk mechanical properties comparable to those of cement concrete [4]. These composites are referred to as ‘carbon concrete’ or C-fix (which stands for Carbon fixation); a cross-section is represented in figure 1.2, with mineral particles, in decreasing order of size: aggregates, filler and sand.
Figure 1.2: A cross-section of C-fix.

C-fix combines the good mechanical properties of cement concrete with the low water adsorption, high chemical resistance and ease of processing and recycling of asphalt [3].

1.1 Environmental Aspects of C-fix

Producing C-fix potentially reduces two sources of carbon dioxide (CO₂) with a negative environmental impact: one resulting from heavy fuel stream burning, another from production of cement concrete.

During production of cement concrete, limestone or chalk (calcium carbonate) is converted (by heating) to calcium silicate. In this process CO₂ is produced, according to the reaction:

\[ 5\text{CaCO}_3 + 2\text{SiO}_2 \rightarrow (3\text{CaO,SiO}_2) + (2\text{CaO,SiO}_2) + 5\text{CO}_2. \]  

1.2 Constituents of PVR binders

PVRs are produced by vacuum distillation of crude oil. In the distillation process most volatile components are removed. PVRs are a complex mixture of heterogeneous species with different molar mass, aliphatic and aromatic nature, and polarity. They can be fractionated into two distinct components, namely maltenes and asphaltenes [5], soluble and insoluble in n-heptane, respectively. Asphaltenes confer elasticity, strength and adhesion to the residue when used as a binder [5].

Asphaltenes are described by Yen [6] as heterocyclic aromatic sheets, associated to form stacks, which in turn may form clusters peptized by a surrounding resin shell to form ‘micelles’ in the viscous malten phase [7, 8]. The resins attach their polar groups to the asphaltenes and stretch their aliphatic groups outwards to form a steric-stabilization layer around the asphaltenes. The attraction between
asphaltenes and resins results, in addition to Van der Waals forces, from hydrogen bonding through the heteroatoms and dipole-dipole interactions due to the high polarity of both constituents [9]. PVRs can thus be described as a colloidal suspension of micelles in a maltene liquid, c.f. figure 1.3. The colloidal behaviour can be quantified using a colloidal index (CI) defined as [10]:

\[
CI = \frac{\text{Aromatics} + \text{Resins}}{\text{Saturates} + \text{Asphaltenes}},
\]

where a higher CI means that the asphaltenes are more peptized by the resins. Maltenes may further be fractionated—with decreasing molecular weight and polarity—into resins, aromatics and saturates [11]; the resins and aromatics provide ductility, whereas the saturates increase fluidity [12].

![Diagram of PVRs structure](image)

**Figure 1.3:** Model of the structure of PVRs. An asphaltene core is surrounded by a resin shell in a viscous maltene phase. Two states are visible, a sol- and gel-state.

### 1.3 Asphaltene association

Depending on whether the micelles can move independently with respect to each other or are interconnected to form a network structure, the binder is called a sol-type binder or a gel-type binder,
respectively. Gel-type binders behave highly non-Newtonian and form when enough asphaltenes and resins are present. Sol-type binders exhibit Newtonian behaviour, i.e. viscosity is independent of the stress and elastic effects are negligible [10, 12, 13]. As a consequence, the ratio between asphaltene and maltene volume fractions is expected to influence the mechanical properties of the binder. This effect is particularly pronounced when the binder is mixed with mineral particles (MP) producing a composite material where self-affine asphaltene aggregates are confined in the 'pore' space between the MP.

1.4 Previous work

In previous work [14, 15] the mechanical behaviour of dispersions of filler particles in C-fix binder was investigated, because the micromechanical behaviour of C-fix binders is closely related to the behaviour of the composite at the macro-scale. Dynamical mechanical analysis (DMA) was performed on different binders mixed with filler particles of different sizes and at various concentrations. By changing the filler size \( d \) and filler fraction \( \varphi \), the inter-particle distance \( A \) could be adjusted. It was demonstrated that when the size of the asphaltene aggregates is of the same order as the inter-particle distance, a percolating network, relying both on the MP and the asphaltene aggregates may arise above a percolation threshold, thus providing rigidity to the composite, c.f. figure 1.4.

![Figure 1.4: Left image: no network visible. Right image: an asphaltene network between mineral particles providing percolation.](image)
The percolation threshold depends on the size and volume fraction of the MP (that determine the pore-size) as well as on the volume fraction of asphaltenes [15].

Scaling according to the modern percolation theory is assumed because a mathematically correct critical scaling exponent $\alpha$ of $3.9\pm0.6$ for the storage modulus $G'$ versus $\varphi - \varphi_c$ was observed, see figure 1.5. This is in good agreement with theoretical values ($\alpha \sim 3.75$) for rigidity percolation [16].

![Figure 1.5: Rigidity percolation in a model composite. The storage modulus $G'$ as a function of the filler fraction minus the critical filler fraction.](image)

1.5 Present study

The question is what makes some residues eligible as C-fix binder and others not. Knowledge on the C-fix microstructure in relation to its mechanical properties is still limited and will be the focus of this work. Surface imaging techniques are used for a better insight on the binder morphology, and how its constituents interact with each other, hence affect the mechanical properties of the composite material. The mechanical properties are measured using nanoindentation and lateral force apparatus. In this study the confinement between mineral particles in a bulk composite is transposed to the confinement within a thin-film, c.f. figure 1.6. In this way the confinement may be adjusted via dedicated coating or deposition techniques and both mechanical testing techniques and surface imaging techniques may be combined to further study the relation between structural and mechanical properties.
1.6 General Overview of project

For a comparative study of microstructure and mechanical properties, two binders are used. These binders have a different asphaltene content.

To characterise the microstructure of the binders, spin-coated binders, and maltene/asphaltene fractions are imaged under an Atomic Force Microscope (AFM). The micromechanical properties are characterised using nanoindentation and friction force measurements. The materials and methods used are described in chapter 2.

In chapter 3 the results and discussion are given for microstructure images obtained by AFM. After the results and the discussion, a brief conclusion of the chapter is given.

In chapter 4 the results and discussion are given for micromechanics measurements obtained by nanoindentation and in chapter 5 the results and discussion are given for micromechanics measurements obtained by LFA. At the end of each chapter a brief conclusion is given.

In chapter 6 the main conclusions are presented for both the microstructure and micromechanics of the binders considered.
Chapter 2

Materials and Methods

2.1 Sample Preparation

2.1.1 Binders

Two petroleum vacuum residue (PVR) binders designated as B38 and B56, provided by Shell, were considered in this work. They differed in origin and cracking severity. B56 originated from low-sulphur European crude's, while B38 originated from high-sulphur Middle East crude.

In table 2.1 the characteristics of the binders used in this study are presented. B38 and B56 contain 24.9 w% and 12.6 w% asphaltenes, respectively. This difference is expected to significantly influence the microstructure and micromechanics of the two binders. Only B38 proved suitable for producing composites with high fracture toughness comparable to that of cement concrete [15].

<table>
<thead>
<tr>
<th>Binder</th>
<th>( \rho ) [g/cm(^3)]</th>
<th>Asphaltenes [w%]</th>
<th>NB.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B38</td>
<td>1.094</td>
<td>24.9</td>
<td>High fracture toughness</td>
</tr>
<tr>
<td>B56</td>
<td>1.047</td>
<td>12.6</td>
<td>Low fracture toughness</td>
</tr>
</tbody>
</table>

Table 2.1: Characteristics of the binders used.

2.1.2 Fractionation

Fractionation of the two binders to yield their asphaltene and maltene constituents was performed by dissolving 5 gram of binder in 200 ml of \( n \)-heptane and keeping the solution in an oil bath at 80\(^\circ\)C for two hours. The solution was then filtered using two superposed paper filters, on which the \( C_7 \)-asphaltenes deposited as a brown powder. Heated \( n \)-heptane (~80\(^\circ\)C) was further poured onto the deposited asphaltene powder, until the drained \( n \)-heptane would become colourless to dissolve any remaining maltene. The maltene solution in \( n \)-heptane was left uncovered under a fume-hood to let the solvent evaporate. Both the maltene and asphaltene were preserved for further analysis.
2.1.3 Spin-Coating

Thin-films were prepared by spin-coating the material to characterise in solution on a glass substrate (soda-lime glass: \( E=72.5 \) GPa and \( H=5.4 \) GPa [17]). The solutions were prepared by dissolving either binder, asphaltene or maltene in toluene at different concentrations. A weight balance with a sensitivity of 0.1 mg was used to measure the weight content of both solute and solvent. After mixing with a magnetic stirrer the solution was filtered using a fine (0.2 µm pore size) filter. Glass slide substrates were cut with a diamond knife after which they were cleaned in an ultrasonic bath with soap and water and further rinsed with distilled water and ethanol. The solution was spread over the substrate and thin-films of different thicknesses were produced using a spin-coater. In figure 2.1 a schematic representation of the spin-coating process is given. A drop of solution is applied to the substrate that is accelerated to a particular speed. The solution flows under the centrifugal force and eventually covers the entire surface. The solution in excess is removed (spin-off) and after evaporation of the solvent a film of uniform thickness is formed.

![Figure 2.1: Schematic representation of spin-coating process. First three stages (deposition, spin-up, spin-off) are sequential, while spin-off and evaporation overlap.](image.png)
Both the spin-coater rotation speed and binder concentration in toluene determine the film thickness. Meyerhofer [18] states that the film thickness $h$ is dependent on the rotation speed $f$, the initial viscosity $\nu_0$ and the evaporation rate $e$ according to

$$h \propto f^{-\frac{2}{3}} \cdot \nu_0^{\frac{1}{3}} \cdot e^{\frac{1}{3}},$$

(2.1)

with $e$ proportional to $f^{\frac{1}{2}}$. Therefore, the film thickness is only dependent on rotation speed $f$ and initial viscosity $\nu_0$ as

$$h \propto f^{-\frac{1}{2}} \cdot \nu_0^{\frac{1}{3}}.$$

(2.2)

This principle is used to make films with different thickness $h$. Concentrations were varied from 2 to 50 w% and the rotation speed between 400 and 5000 rotations per minute (rpm) for 120 seconds. Initial acceleration was set to 2000 rpm/s. Thicknesses are given in table 2.2.
<table>
<thead>
<tr>
<th>Sample label</th>
<th>Solution of binder in toluene [wt%]</th>
<th>rotation speed spin-coater [rpm]</th>
<th>B38</th>
<th>B56</th>
<th>maltene from B38</th>
<th>maltene from B56</th>
<th>asphaltene from B38</th>
<th>asphaltene from B56</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>500</td>
<td>110</td>
<td>760</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>5000</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>500</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1000</td>
<td>1000</td>
<td></td>
<td></td>
<td>250&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td>220&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>2000</td>
<td>2000</td>
<td></td>
<td></td>
<td>170&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td>170&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>3000</td>
<td>3000</td>
<td></td>
<td></td>
<td>120&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td>120&lt;sup&gt;AFM&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>4000</td>
<td>4000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>5000</td>
<td>5000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>20</td>
<td>500</td>
<td>3000</td>
<td>3300</td>
<td>1000</td>
<td>1500</td>
<td>5000</td>
<td>3300</td>
</tr>
<tr>
<td>L</td>
<td>5000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>50</td>
<td>300</td>
<td>1100</td>
<td>700</td>
</tr>
<tr>
<td>M</td>
<td>400</td>
<td>400</td>
<td>14000</td>
<td>7000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>500</td>
<td>500</td>
<td>12000</td>
<td>5500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1000</td>
<td>1000</td>
<td>10000</td>
<td>8000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>2000</td>
<td>2000</td>
<td>8000</td>
<td>6500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>3000</td>
<td>3000</td>
<td>7000</td>
<td>6000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>4000</td>
<td>4000</td>
<td>6000</td>
<td>4500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.2:** Thickness of spin-coated thin-films [nm] used in this study. Thicknesses indicated with <sup>AFM</sup> are measured using an atomic force microscope, other thicknesses are measured using nanoindentation.

Thicknesses of some films were measured via AFM, as indicated in the table. Thickness of the remaining films was determined via nanoindentation experiments, c.f. chapter 4.3.

### 2.1.4 Melted Binders

The maximum thickness achieved with spin-coating of binder solutions is around 14 μm. Because it is difficult to make a solution with a high concentration of binder in toluene (for increased film thickness), thicker films were prepared by means of Doctor Blades. Doctor Blades have a thread that
can be used to produce a thin-film from a drop of material, by sliding over a substrate. Binder was melted on glass substrates heated at 140°C, then spread with the use of Doctor Blades with threads ranging from 4 to 80 μm. This results in films with thicknesses of the same order as the threads of the Doctor Blades.

### 2.2 Atomic Force Microscopy

#### 2.2.1 Introduction

Atomic force microscopy (NanoScope III, Digital Instruments) was used to image thin-film specimen. Topography and phase contrast were measured simultaneously in Tapping Mode. Image processing was usually limited to offset flattening, which consists of subtracting a plane to the image to optimise the contrast without distorting the topographic features.

#### 2.2.2 Set-up

In figure 2.2 a photograph of the AFM is presented, with a schematic of the microscope head.

![Figure 2.2: Left: Photograph of the atomic force microscope and Right: A schematic of the AFM head [19].](image-url)
The AFM constitutes [19]:

- A head where the laser diode and the position sensitive laser detector are situated. Furthermore the head provides optical correction of the laser beam path to position the laser on the cantilever. The head also includes a piezo tube, which allows the tip holder and cantilever to travel in the x-, y- and z-direction.

- A tip holder, which holds the cantilever firmly at the proper angle. The tip holder secures the cantilever with a spring-loaded clip; it contains the electrical contacts for a piezoelectric stack to oscillate the cantilever when operating in Tapping Mode.

- A cantilever with tip. The cantilevers used in this work are provided by MikroMasch. The silicon cantilevers type NSC12/50 are coated on the reflective side with aluminium and the radius of curvature of the tip is less than 10 nm. Three cantilevers are mounted on each side of a silicon chip. In figure 2.3 scanning electron microscopy (SEM) images are given of the silicon cantilever. The cantilever with a length of 250 \( \mu \text{m} \) is used.

![Figure 2.3: SEM images of the silicon cantilever and tip, provided by MikroMasch.](image)

- An optical microscope is used for optical imaging of the scan area during movement of the microscope head in the z-direction. This is done to make sure not to touch the sample and break the tip. The optical microscope can also be used to select a scan area.

- The AFM head is controlled by a complex electronic set-up and relayed by computer software, where topography, phase and other data, measured at the head, are acquired and analysed.

- A vibration isolation table is used to isolate the AFM from ground vibrations and also isolates the AFM from acoustic vibrations using a noise isolation hood.

### 2.2.3 Tip-sample interaction

When the AFM tip is brought in close proximity to a sample surface, the tip interacts with the surface. At the Angstrom level above the surface, Van der Waals forces cause a weak attraction between the
atoms in the tip and sample. This attraction is used to monitor non-contact tip-sample interactions. If the tip and sample are brought closer together the atoms begin to encounter each other's Coulomb force. The electron shells from the atoms of the tip and sample repulse one another, preventing penetration by one material into the other. This repulsion is used in contact mode AFM. In figure 2.4 a force-distance curve can be seen.

![Force-distance curve for tip-sample interaction.](image)

**Figure 2.4:** Force-distance curve for tip-sample interaction. The intermittent contact mode is used in this study [20].

### 2.2.4 Tapping mode

The Tapping Mode or intermittent contact mode is used in this work. The cantilever is driven at a frequency just below the resonance frequency. The amplitude of the vibration will increase when bringing the tip closer to the sample, up to the point when during part of the cycle the tip touches the sample. This induces a decrease of the vibration amplitude, which is used to control the tip-sample distance. The short tip-sample contact time prevents inelastic surface modification. Because the binder films are 'soft' samples, tapping mode is the best choice for imaging.

When the tip is scanned across the surface, a tip deflection will result from a change in topography. Therefore, by measuring this deflection, the topography can be inferred. A feedback system is used to keep tip-sample interaction constant. Not only topography but also phase differences can be measured. This works by measuring the phase difference between the oscillations of the cantilever driving piezo and the detected oscillations. It is thought that image contrast is derived from sample properties such as stiffness and elasticity [20].
2.3 Nanoindentation

2.3.1 Introduction

Nanoindentation is used here to measure micromechanical properties—like hardness and elastic modulus—of the considered binders and their asphaltene and maltene fractions.

Indentation tests are commonly used for characterising the mechanical properties of materials. In such a test, a hard tip is pressed into a sample with a known load. After a certain time, the load is removed. The area of the imprint left from the indentation is measured and the hardness, defined as the maximum load $P$, divided by the residual indentation area $A$, can be obtained.

Nanoindentation proved to be an excellent way for measuring mechanical properties at very small volumes of material, i.e. thin-films, coatings and surface layers. In principle, if a sharp tip is used, the contact area between the sample and the indenter tip, thus volume of material, can be made arbitrarily small. The only problem then is determining the indentation area.

To solve this problem depth-sensing indentation methods were developed. In these methods, the load and displacement of the indenter are recorded during the indentation process and these data are analysed to obtain the contact area without having to see the indentations.

The nanoindentation technique refers to depth-sensing indentation at the sub-micron range, and has been made possible by the development of:
1. machines that can make small (<100 nm) indentations while recording load and displacement with high accuracy, and
2. models to interpret load-displacement data to obtain hardness, elastic modulus and other mechanical properties.

2.3.2 The nanoindenter

Nanoindentation experiments were carried out on a load-controlled Nanoindenter XP (MTS Nano Instruments, Oak Ridge, Tennessee), using the continuous stiffness measurement (CSM) option. The Nanoindenter XP combines in principle of: A means for applying a known load, a means for measuring the resultant displacement with sufficient accuracy and a means to position the indenter tip over the sample.
Figure 2.5: Schematic of the nanoindenter [21].

In figure 2.5 a schematic of the nanoindenter is given [21]. It consists of a coil/magnet assembly, support springs, a capacitive displacement gage, an indenter and a motorised stage.

The load is imposed on the indenter by passing a current through a coil that sits within a circular magnet. By varying the current $I$ through the coil, a magnetic field is generated that interacts with the magnetic field of the permanent magnet (just like in a speaker). In this way, the load imposed on the indenter shaft is directly proportional to the current passing through the coil.

The support springs are designed to have a very low stiffness in the vertical direction and very high stiffness in the horizontal direction. This makes the springs to hold the indenter shaft very accurately at a certain place, without changing the load on the sample to much.

Because the indenter is normally load-controlled, the displacement is only measured and not controlled. For the measurement of the displacement a three-plate capacitive gage is used, where the outer plates are fixed and the center plate is mounted on the indenter shaft. The center plate can move freely in the vertical direction between the two outer plates. The position of the center plate, thus indenter shaft, is determined by the difference in current between the top plate and center plate and the bottom plate and center plate. As a charge is placed on one of the plates, a current will flow across the cap between the plates. The amount of current that flows across the gap is determined by the voltage, the area of the plates, the material that separates the plates and the distance between the plates.
That is:

\[ Q = C \ast V \]  \hspace{1cm} (2.3)

and

\[ C = K \ast \varepsilon_0 \ast A / d \]  \hspace{1cm} (2.4)

with \( C \) the capacitance, \( V \) the voltage, \( Q \) the current, \( K \) the dielectric constant, \( \varepsilon_0 \) the permitivity of free space, \( A \) the area of the plates and \( d \) the distance between the plates.

Because the voltage, area of the plates and material between the plates are held constant all changes in current are due to changes in the distance between the plates.

The indenter consists of an indenter shaft and tip which is held in place by a retaining collar in the indenter shaft. The most commonly used indenter tip geometry is the Berkovich indenter: It consists of a three-sided pyramid made from diamond as can be seen from figure 2.6. A Berkovich tip is normally used because it produces plasticity at very low load, it has a good manufactured quality and it minimises the influence of friction.

![Berkovitch indenter tip](Image)

**Figure 2.6:** Schematic representation of a Berkovich indenter tip (right) and residual imprint (left) [21].

The last part of the indenter is a motorised stage. With this stage, desired indentation sites can be selected by observing the surface through an optical microscope. The stage is then automatically translated to bring the site to the indenter tip. The stage is screw-driven and an accuracy for site selection of around 1.5 \( \mu \text{m} \) can be obtained.
The indenter is isolated from acoustic vibrations and temperature changes by a Minus K vibration isolation table and an isolation cabinet.

The Minus K negative stiffness vibration isolation table is an active system and uses a spring to support the load on the table and two additional springs that are loaded against the main support spring in the horizontal direction. These springs have a tendency to buckle in the direction of a deflection, which increases as the preload on the springs is increased. This creates a ‘negative stiffness’. By tuning the preload on these springs, this negative stiffness can be balanced against the main support spring. Adjustment of the main support spring can be made to ensure that the payload is floating in the center of the vertical travel of the table.

The isolation cabinet is used to provide a stable air mass in which sudden temperature changes should be minimised. The foam on the interior of the cabinet absorbs acoustic energy.

The continuous stiffness measurement (CSM) mode used in this study allows a continuous measure of the stiffness during loading, thereby allowing a calculation of the hardness and elastic modulus as a continuous function of indentation depth. This is done by employing tiny modulations on a mean loading displacement with, for all measurements in this thesis, a frequency of 75 Hz.

The resolution of the Nanoindenter XP for the measured displacement and load is \(2 \times 10^{-13}\) m and \(1 \times 10^{-9}\) N, respectively. The frequency range for the CSM is 0.1 Hz to 300 Hz and the resonant frequency of the indenter is 180 Hz.

The samples were mounted on aluminium stubs, of 1¾ inch in diameter and 1 inch in height, by means of double-sided tape; glue or holding screws could also be used. This aluminium stub was then placed into the sample tray and loaded onto the motorised stage.

2.3.3 The Oliver-Pharr method

From the load-displacement data collected by the nanoindenter, mechanical properties of the sample can be determined. With the nanoindentation technique one can obtain much more information than just hardness. However the results obtained depend on the analysis model chosen.

In figure 2.7 a typical load-displacement curve is shown. As the load is increased, the indenter is driven into the material due to elastic and plastic deformation. As the load is held constant, the indenter continues to sink into the material due to creep. As the indenter is withdrawn, primarily the elastic portion of the displacement is recovered. This recovery allows one to determine the elastic properties of a material. The hardness impression left is due to the plastic component of the displacement.
Important quantities are peak load and displacement, $P_{\text{max}}$ and $h_{\text{max}}$, the residual depth after unloading, $h_f$ and the slope of the initial portion of the unloading curve, $S = dP/dh$.

The model used in this work is known as the Oliver-Pharr method [22]. It is an extension of the method proposed by Doerner and Nix [23] and accounts for the fact that unloading curves are distinctly curved and cannot be modelled by a flat punch approximation. The Oliver-Pharr method is the most successful and widespread for nanoindentation data analysis and assumes that only the elastic portion of the displacement is recovered. The model is designed for monolithic materials that sink-in and begins by fitting the load-displacement data acquired during unloading to the power law relation

$$P = B(d - h_f)^m,$$  \hspace{1cm} (2.5)

where $P$ is the applied load, $d$ the displacement into the sample, $B$ and $m$ are empirically determined fitting parameters and $h_f$ is the final displacement after complete unloading. The unloading stiffness $S$ is then given by analytically differentiating (2.5) and evaluating at the maximum displacement into the sample $d = h_{\text{max}}$, so

$$S = \frac{Bm(d - h_f)^{m-1}}{d = h_{\text{max}}}.$$  \hspace{1cm} (2.6)
The contact depth $h_c$ is given as

$$ h_c = \Delta l - \epsilon \frac{P}{S} \quad (2.7) $$

with $P$ the load on sample, $S$ the harmonic contact stiffness and $\epsilon=0.75$ for a Berkovich indenter. $\Delta l$ represents the displacement into the sample $d$ minus the displacement before the tip reaches the specimen surface $d_0$.

Finally, the contact area is calculated using an area function, which is given for a Berkovich indenter by

$$ A(h_c) = 24.5h_c^2 + \sum_{i=0}^{7} a_i \cdot h_c^{1/2} , \quad (2.8) $$

where the first right-hand term gives the contact area for an ideal indenter and the following terms represent the geometrical deviations due to tip rounding.

Once the contact area is determined, the hardness is estimated from

$$ H = \frac{\Delta P}{A} \text{, where} \quad (2.9) $$

$$ \Delta P = P(d) - P(d_0) \quad (2.10) $$

$\Delta P$ represents the load on the sample minus the load on the sample at zero displacement into the sample. Note that this definition of hardness is based on the contact area under load, and may deviate from traditional hardness measurements where the area of residual impression is used. This deviation is significant for materials with high elastic recovery during unloading.

The reduced modulus follows from its relationship with the harmonic contact stiffness and the contact area and is given by

$$ E_R = \frac{\sqrt{\pi} S}{2\beta \sqrt{A}} \quad (2.11) $$
with $S$, the harmonic contact stiffness, or the slope of the unloading curve $(dP/dh)_{unload}$ and $\beta$ a dimensionless parameter related to the geometry of the indenter. For a Berkovich indenter $\beta=1.034$.

The reduced modulus takes into account the fact that both the tip and the sample undergo elastic displacements. The elastic modulus within the sample can then be calculated from

$$\frac{1}{E_R} = \left(1 - v^2\right) + \left(1 - v_i^2\right) \frac{E \cdot E_i}{\left(E \cdot E_i - 1\right)} \quad (2.12)$$

with $v$ the Poisson’s ratio of the sample, $v_i$ the Poisson’s ratio of the indenter tip and $E_i$ the elastic modulus of the indenter. The elastic modulus and Poisson’s ratio of the indenter tip are known and reported in the literature for a diamond tip as $E_i=1016$ GPa and $v_i=0.07$ [24].

### 2.3.4 Issues related to nanoindentation

#### 2.3.4.1 Substrate effect

With nanoindentation, thin-films may be characterised by measuring locally their mechanical properties without removing the film from the substrate. However, the indentation response reflects both film and substrate properties and these have to be distinguished carefully [25] [26]. It is generally assumed that properties most representative of the layer are obtained at an indentation depth around 10% of the film thickness [22, 25, 26, 27]. This rule may not apply for films with a thickness in the sub-micron range (<100 nm), as the indentation is then only a few nanometers deep. At this scale vibration and non-uniform indenter tip geometry become important and accurate measurements are difficult to obtain. Consequently, for such films nanoindentation can only be used in a qualitative sense.

#### 2.3.4.2 Pile-up

Another issue related to nanoindentation is to what extent material ‘pile-up’ affects the measured material properties. This issue pertains to the use of an elastic contact analysis to determine the contact depth thus the contact area. Because materials that deform elastically always ‘sink-in’, pile-up is not properly accounted for [28]. Pile-up can be attributed to the viscoelastic nature of the material and phenomena such as adhesion of the material to the indenter tip or flow of material to the surface caused by an undeformable substrate where plastic flow is restricted.
2.3.4.3 Surface smoothness

Surface smoothness is important because the contact area is calculated from the contact depth and the area function rather than observed directly. Thus, the degree of required smoothness depends on the indentation depth and the tolerance for uncertainty in the contact area. From AFM scans there has been confirmed that the spin-coated films used are sufficiently smooth (roughness in the order of nanometers) for nanoindentation.

2.3.4.4 Initial point of contact

Defining the initial point of contact between the indenter and the sample is the starting point in the analysis of indentation data. Parameters that affect the accurate determination of the location of this point are the data acquisition rate, indentation speed and the resolution in the load and displacement. To determine the initial point of contact the entire mechanical behaviour of the system is observed before, during and after the initial point of contact. Afterwards the initial point of contact is identified by observing the behaviour of the load and the stiffness.

2.3.5 Operation of the Nanoindenter

The indenter was operated in continuous stiffness measurement (CSM) mode and at constant strain rate. Twelve indentations at 100 μm intervals were performed on each sample. After the tip approached the surface of the sample at 10 nm/s, indentations were made at a constant strain rate of 0.05 s⁻¹ by controlling $\dot{P}/P$, where $\dot{P}$ and $P$ are load rate and load, respectively. The tip shape was calibrated following the procedure as described by Oliver and Pharr [22] using fused silica as a reference material.

Parameters measured during nanoindentation were exported and post-treated as an MS Excel datasheet. The displacement into the surface, load on sample and harmonic contact stiffness were used to calculate the hardness and elastic modulus.

The elastic modulus and hardness were calculated for up to twelve indentations then averaged over the whole batch of measurements. The error was estimated from the standard deviation ($\leq 10\%$) and the pile-up of material. No error in the mechanical properties could be determined due to creep. Although creep is present in binders, it should have no effect on the mechanical properties measured, because indentations were made using a constant loading rate, thus a constant strain rate [46].

21
2.4 Lateral Force Apparatus

2.4.1 Introduction

To further study the relationship between the structure and the mechanical properties of the binder a second technique that relates the friction force between a tip and a thin-film with the thin-film structure is used. This technique is applied using a Lateral Force Apparatus (LFA).

2.4.2 Experimental set-up

The Lateral Force Apparatus (LFA) used for this project, is a home-built device developed to relate the structure of polymers to their mechanical properties. It uses a hard single asperity (tip) for scratching a sample and allows independent measurement of lateral and normal forces between tip and sample. The friction coefficient indicates the resistance of a material to tip penetration in the lateral direction.

![Figure 2.8: Schematic drawing of Lateral Force Apparatus [29].](image)

In figure 2.8, a schematic representation of the LFA is shown. The LFA consists of a leaf-spring unit on which a probe tip is attached. The leaf-spring unit uses leaf springs in the lateral and normal direction with in principle independent bending modes. The leaf-springs that probe the normal force...
are situated in between the lateral force leaf springs, as shown in figure 2.8. A cantilever with normal stiffness, \( k_n \sim 320 \text{ N/m} \) and lateral stiffness, \( k_l \sim 240 \text{ N/m} \) was used. The cross talk between the normal and lateral leaf springs was in the order of 1% and the probe tip used had a radius of 50 \( \mu \text{m} \).

A second part of the set-up consists of the optical focus error heads. This type of sensor measures the deflection of the leaf-springs by guiding a laser beam from a laser diode grating unit (LDGU) to the object surface. The reflected beam is transmitted back into the LDGU. The deflection measured by the LDGU is a measure for the force on the leaf-spring (given the spring constants, which are measured by nanoindentation).

The optical focus error heads and the leaf-spring unit are both mounted on an aluminium frame with one degree of freedom, along the z-axis. The z-position can be controlled using a piezo actuator suitable for dynamic applications.

The sample stage can move in both the x- and y-direction. In the x-direction (direction of scratching, thus friction) the movement is controlled by a DC motor, while the y-direction is controlled by a micrometer head to guide the tip to a new scratch track. The coarse positioning in the z-direction is controlled by another micrometer head.

A thorough description of the LFA and an operation instruction can be found elsewhere [29, 30]. Experiments done on the LFA are so-called slide-hold-slide experiments, c.f. figure 2.9.

![Graphs](image)

**Figure 2.9:** Typical curves of slide-hold-slide experiments; speed, friction force and normal displacement versus time. During hold period, the tip sinks into the material with \( \Delta z \). After the hold period, there can be seen a maximum friction force, \( F_{\text{max}} \).
In this type of experiments a normal force is applied to the tip. After applying a normal force, $F_N = 2.5 \text{ mN}$, the tip moved with a velocity, $v$, over a distance of $100 \mu\text{m}$. The motion is held for a certain holding time, $t_h$, after which it is resumed at the same velocity, $v$, over a distance of $100 \mu\text{m}$. The steady state friction force, $F_r$, is derived from averaging the friction force over the sliding time after the initial friction force peak $F_{\text{max}}$. 
Chapter 3

Atomic Force Microscopy

3.1 Introduction

In this chapter thin-films of binder and their maltene and asphaltene fractions were imaged using AFM. The microstructural changes due to heating for both binders, and microstructural differences between melted binders and spin-coated binders were also investigated via AFM. These experiments are done to get a better understanding of the morphology of the binders used and their constituents, as well as the interactions between the different constituents of the binders.

3.2 Different Binders

In figure 3.1 the morphology of B38 binder can be seen as a function of the film thickness (AFM scan in phase contrast). The binder is spin-coated on a glass substrate. From figure 3.1 it can be seen that the asphaltene domain area (light area) increases with increasing film thickness, eventually covering the whole surface at a film thickness of around 3 μm. After complete coverage the asphaltene domains retract with increasing film thickness, yet still appearing at a film thickness of 10 μm.

As the domains increase in size, two ‘growth modes’ can be observed. The first is characterised by an increase in domain size with increasing thickness. The second ‘mode’ is characterised by the formation of domain clusters that form ‘flower’ patterns.

Simultaneously, paraffin wax crystallises from the edges of the asphaltene domains (seen as darker areas), and grows —both in surface and in height— on top of the asphaltene domains. The wax eventually covers almost the whole asphaltene domain. The paraffin wax may form by condensation of the saturate fraction [31] of the binder. The paraffin wax may nucleate on the aliphatic side-chains of the resin, then grow on top of the —high surface energy— asphaltene domains [32].

The occurrence of scan lines on AFM scans is associated with smearing of the maltene phase by the tapping tip [33].
Figure 3.1: AFM scan of B38 thin-films versus film thickness (phase contrast). Given are the concentrations of solutions used and the spin-coating speeds.
In figure 3.2 the morphology of B56 binder as a function of film thickness is presented (AFM scan in topography and phase contrast). The binder is spin-coated on a glass substrate. From figure 3.2 it can be seen that the B56 binder asphaltene domain area (presented as dark area in the topography image) increases with increasing film thickness, eventually covering the whole surface at a film thickness of around 4.5 μm. As the film thickness further increases, the domain size gets smaller, but the domains continue covering the whole surface and do not retract as on B38 films.

For B56 the asphaltene domains seem independent, not forming clusters. This suggests that only one 'growth mode' is present. This lack of interactivity may allow B56 asphaltenes to migrate freely to the surface forming a 'curd' on top of the maltene phase. As the thickness increases, a thicker and denser 'curd' may form, reflected by smaller domains. The paraffin wax outgrowth seen in B38 thin-films is absent on B56 thin-films.

![AFM scan of B56 thin-films versus film thickness. Top image: topography and Bottom image: phase contrast. Concentrations of solutions and spin-coating speed are given.](image)

**Figure 3.2:** AFM scan of B56 thin-films versus film thickness. Top image: topography and Bottom image: phase contrast. Concentrations of solutions and spin-coating speed are given.
3.3 Asphaltene

In figure 3.3, high resolution AFM scans on asphaltene thin-films are presented. The asphaltenes appear as porous, as reported by Espinat [34] and Loeber [35] and the shape is irregular. Asphaltene fractionated from B38 and B56 slightly differ in mesh size: for asphaltene fractionated from B38 the mesh size is between 50 and 100 nm, whereas for asphaltene fractionated from B56 the mesh size is around 10 to 50 nm. This range is consistent with results found in literature [34, 36].

![Topography and Phase Contrast of Asphaltene Thin-Films Fractionated from B38 and B56](image)

**Figure 3.3:** High resolution AFM scan (Left: topography and Right: phase contrast) of asphaltene thin-films fractionated from B38 (Top) and B56 (Bottom) binder. Thin-films made with a 5% solution at 5000 rpm.

It has also been observed that a ‘skin’ overlays the asphaltene network on the phase contrast image. This ‘skin’ can be penetrated by tapping harder on the surface with the AFM tip.
3.4 Maltene

In figure 3.4, AFM scans on maltene thin-films fractionated from B38 and B56 in phase contrast are presented as a function of film thickness. In the maltene phase, domains still appear. Resins and/or lower molecular weight asphaltenes (so-called C$_5$ asphaltenes)—$n$-heptane soluble, thus present in the maltene phase—could still form micelles even deprived of high molecular weight asphaltenes (so-called C$_7$ asphaltenes), c.f. Li et al. [37].

From figure 3.4, it can be seen that the thin-films of maltene fractionated from B56 are thicker and the domain size is larger than maltene thin-films fractionated from B38 at identical spin-coating conditions. On the thickest films fractionated from B38 again waxes form in the shape of diamond crystals, as described by Srivastava et al. [38].

Figure 3.4: AFM scan of maltene thin-films fractionated from B38 and B56 versus film thickness (phase contrast).
3.5 Asphaltene and maltene

On a closer look at the interface between the continuous phase and the domains, shown in figures 3.1 and 3.2, the asphaltene domains appear as a network embedded in the (oily) maltene phase, c.f. figure 3.5. The asphaltene phase appears as an irregularly shaped network, whereas the maltene phase appears as a smooth phase [10].

![Topography and Phase Contrast](image)

**Figure 3.5:** High resolution AFM scan (topography and phase contrast) of a B56 thin-film (5% solution, spin-coated at 4000 rpm). The asphaltene network and maltene smooth phase can be seen.

3.6 Discussion of results on spin-coated binders

From the results above the maltene phase appears as a smooth phase on AFM scans, whereas the asphaltene phase appears as a porous phase that forms domains.

![Depth Profile](image)

**Figure 3.6:** 'Depth profile' of B38 and B56 thin-films. For B38 the domains retract after a maximum is reached, whereas for B56 the domains cover the entire surface at large film thicknesses.
Figure 3.6 represents a ‘depth profile’ for both B38 and B56 thin-films spin-coated on glass substrates built from successive AFM scans of thin-films with increasing thickness: the domain area is plotted versus the film thickness. It suggests a limited range for asphaltene domain growth in B38 binder, whereas for B56 the asphaltene domains seem to ‘float’ on the maltene phase.

From the observations presented in figures 3.1, 3.2 and 3.6, the following schematic of asphaltene growth in thin-films made of B38 and B56 binder can be drawn, presented in figure 3.7. For B38 unlike B56 thin-films, the asphaltenes form clusters and paraffin wax is formed on top of the domains. It seems that for B38 thin-films the asphaltenes adhere to the substrate (suggested by the limited range for asphaltene domain growth), whereas for B56 thin-films, the asphaltene domains seem to float (suggested by persistent coverage for asphaltene domain).

![Diagram](image)

*Figure 3.7: Schematic representation of asphaltene domain growth in thin-films of B38 and B56 binder.*

The following remarks should be related to the results presented above to explain the differences between thin-films made of B38 and B56 binder. There must be kept in mind that B56 has less asphaltene than B38, but a higher colloidal index, which means that the asphaltenes are more peptized by the resins. B56 is a sol-type binder, whereas B38 is a gel-type binder.
Resins help to solubilize the asphaltenes by forming a resin-solvated asphaltenic aggregate and thus tend to diminish the surface-active nature of the asphaltenes [32]. The addition of resins to asphaltenes reduces the aggregate size by disrupting the π-π and polar bonding interactions between asphalene monomers. Interaction between resins and asphaltenic aggregates makes the aggregates less surface-active [39].

The interaction between asphaltenes and neutral surfaces of kaolinite (layered silicate composed of silica and alumina sheets) was investigated through molecular dynamics calculations by Murgich et al. [40]. They found the Van der Waals interaction to have the largest contribution, i.e. 60-70%, while the Coulomb interaction only contributes 20-30% to the asphalene-surface interaction. Priyanto et al. [41] and Branco et al. [42] found that asphaltenes have an adsorption affinity to solid surfaces.

Previous work done by Puig et al. [43] on the two binders here considered (B38 and B56) found a higher dispersive surface energy (the non-specific contribution to the binder surface energy) compared to the B56 binder, due to difference in asphaltene content.

### 3.7 Hot Stage

The effect of elevated temperature was investigated on both B38 and B56 binders. For each binder two films of different thickness were submitted to a temperature stage (Linkam Scientific Instruments LTD., Surrey, England) as seen in figure 3.8. Thin-films were heated at a rate of 20°C/min up to 60°C and kept at this temperature for 2 minutes in the first stage. In the second stage the samples were heated to 120°C and kept at that temperature for 2 minutes. After the stages, the samples were cooled down to room temperature and observed under an AFM.

![Figure 3.8: Schematic of temperature stages. AFM images were taken after cooling to room temperature.](image)

In figure 3.9, AFM scans of B38 thin-films are presented. Both topography and phase contrast scans are shown of the binder at room temperature and elevated temperatures.

On films prepared from 5% solution (thinner film), as the temperature increases to 60°C, the asphaltenic domains show a tendency to link. This may be due to a higher mobility of the asphaltenes in the maltene phase at this temperature. The asphaltenes then tend to interact and form elongated
clusters. A ridge can also be seen, which may form due to constrains upon solvent evaporating or temperature changes. At 120°C, the large domains break up into smaller, similar to those observed on B56 thin-films.

On films prepared from 50% solutions (thicker film), as the temperature rises to 60°C, the asphaltene domains break up into smaller isolated domains. At the same time, wax crystals grow from the edges of the domains. As the temperature further increases to 120°C, the domains decrease in surface size and tend to link (as for 5% solution at 60°C).

![AFM scan of a B38 thin-film exposed to temperature stages](image)

**Figure 3.9:** AFM scan of a B38 thin-film exposed to temperature stages (Top: topography and Bottom: phase contrast) as presented in figure 3.8. Films prepared from 5% (Top) and 50% (Bottom) solution.

These observations suggest a parallel between the 5% and 50% solution B38 films with a shift of 60°C. This parallel could be related to the heat capacity of the films: a thicker film may require
additional heat to produce the same effect observed in a thinner film. It may also be related to a higher mobility of asphaltenes in a thicker film.

It was observed by Spiecker et al. [45] that heating asphaltenes to 53°C was only effective in reducing the aggregate size of the asphaltenes if aggregation was stabilised through π-π bonding. Heating to 53°C was ineffective in disrupting stronger polar and hydrogen-bonding forces that dominate self-aggregation. When the asphaltenes were heated from 25°C to 80°C they found a large reduction in aggregate size for asphaltenes from four different crude-oils. The results of Spiecker et al. are in agreement with our observations, where we see a decrease in aggregate size as the temperature is increased to 120°C.

In figure 3.10, AFM scans of B56 thin-films are presented under the same conditions as the B38 AFM scans. For films prepared from 5% solution (thinner film), as the temperature rises to 60°C, the asphaltene domains seem to grow. A ‘shell’ is formed around the asphaltene domains, seen both on topography and phase contrast images. As the temperature is further increased to 120°C the domains form clusters, similar to the clusters found on B38 thin-films (the ‘flower’ pattern). This may be due to the elevated temperature, which causes a higher mobility for the asphaltenes.

For films prepared from 50% solution (thicker film) the effects of elevated temperature are distinct. As the temperature increases to 60°C, the domains grow in size and show a better defined structure. The domain walls are clearly visible and ‘fringes’ have formed in the domain centres. At a temperature of 120°C the domains have grown to 15 μm in size and the structure, seen at a temperature of 60°C, is less defined in the phase contrast image, but more defined in the topography image. The ‘fringes’ formed have also grown in size. These ‘fringes’ may be the result of mechanical constrains upon cooling.
An opposite behaviour is observed for asphaltene domain growth upon heating for the two binders under consideration. For B38 films, an increase in temperature causes a decrease in asphaltene domain size, whereas for B56 the opposite happens. This can be explained by the difference in colloidal state thermodynamical behaviour.
3.8 Melted Binders

Besides spin-coating, spreading of melted binder on glass substrates with Dr. Blades was also available to prepare thin-films, giving access to much thicker films (up to 80 μm). In figure 3.11, AFM scans in phase contrast of B38 and B56 binder melted on glass are presented.

Figure 3.11: AFM images of melted binders versus thickness film (Dr. Blade) for both B38 and B56 films. Left: Topography; Right: Phase contrast.

Figure 3.11 shows that on B38 films, domains around 5 μm wide are formed. In B56 binder, domains about 5 to 10 μm wide are formed with fringes visible in each domain. As B38 has a high asphaltene content and low colloidal index (gel-type), the asphaltenes associate. For B56 with a low asphaltene content and high colloidal index (sol-type), the asphaltenes form domains surrounded by the oil phase [7].

The microstructure observed for the melted binders is typical for all samples irrespective of the film thickness, whereas the microstructure observed for spin-coated binders is influenced by the film thickness, c.f. figures 3.1 and 3.2. The mesh size of the asphaltene network for melted binders (5-10 μm) is two orders of magnitude larger than for spin-coated asphaltenes (10-100 nm).
3.9 Conclusions

From the measurements done on the microstructure of binders and their constituents, there can be concluded that more insight into the morphology of the binders is obtained. From the AFM images, asphaltene domains and the maltene phase could clearly be distinguished for both binders. For B38, asphaltene domains form clusters and paraffin wax crystallises on top of the asphaltene domains. For B56, asphaltene domains seem independent and no paraffin wax is formed. The asphaltenes in B38 are more reactive and have a tendency to interact with their surroundings.
Chapter 4

Nanoindentation

4.1 Introduction

In this chapter results are presented of thin-films indented using a MTS Nano Instruments Nanoindenter XP fitted with a Berkovich indenter tip. Both binders and their constituents were indented to characterise their mechanical properties. So as to get a better insight on the mechanical properties of the binders and their constituents, but also in conjunction with the findings in the previous chapter, to have a better understanding of the relationship between the binder morphology and its mechanical properties.

4.2 Hardness and Elastic Modulus

From the load-displacement curve acquired during indentation, hardness \( H \) and elastic modulus \( E \) are determined for films of differing constitution and thickness. Results are presented as a function of scaled indentation depth \( d/h \), with \( d \) the indentation depth and \( h \) the film thickness. For a perfect Berkovich indenter and in the absence of effects related to a characteristic lengthscale, \( d \) and \( h \) are the only characteristic lengths present, and \( d/h \) is expected to scale the results obtained. Deviations from this expected scaling behaviour for the binders may show the confinement effect that has been encountered in bulk mineral-filled binders [15]. However, other possible sources of deviation from the scaling behaviour need to be excluded.

The elastic modulus \( E \) and hardness \( H \) were measured and plotted as a function of the indent depth \( d \) scaled to the film thickness \( h \) (figures 4.1a to 4.3b). An abrupt increase in the hardness is noticeable as the indenter contacts the glass substrate: the corresponding indent depth has therefore been chosen as a measure for the film thickness (i.e. \( d/h=1 \)). Additionally, the elastic modulus should present an inflection point near the interface between the film and the substrate. This was validated on the sub-micron films by AFM (series of scalpel scratches). When the indent depth was too shallow for the indenter to reach the substrate, the abrupt hardness increase/ elastic modulus inflection point had to be extrapolated.
Figures 4.1a and 4.1b: Elastic modulus and hardness versus scaled indentation depth for binders B38 and B56. Codes A to R—for solution and spin-coating speed used—can be found in chapter 2.1.2.

In figures 4.1a and 4.1b both the elastic modulus and hardness for the two different binders are plotted as a function of the indentation depth scaled to the film thickness. The elastic modulus $E$ and the hardness $H$ present both an initial decrease as the indenter penetrates the surface of the thin-film down to a minimum typically at $d/h \approx 0.1$; subsequently, the elastic modulus and hardness increase towards the values for the soda-lime glass substrate (72.5 GPa and 5.4 GPa, respectively [17]).
Figures 4.2a and 4.2b: Elastic modulus and hardness versus scaled indentation depth for asphaltene.

Figures 4.3a and 4.3b: Elastic modulus and hardness versus scaled indentation depth for maltene.
The elastic modulus and hardness for thin-films made from asphaltene and maltene solutions are plotted in figures 4.2a and 4.2b and 4.3a and 4.3b, respectively. The $E$ and $H$ versus $d/h$ for thin-films prepared from asphaltene (maltene, respectively) solutions show similar trends as films prepared from B38 (B56, respectively) solutions. For both B38 and asphaltene thin-films, the trend for $E$ and $H$ is an initial decrease and a broad minimum followed by a smooth increase towards the substrate’s $E$ and $H$. As for B56 and maltene thin-films the trend for $E$ and $H$ is a decrease and an abrupt transition to the substrate’s $E$ and $H$.

The question is of which value on the $E$ and $H$ versus $d/h$ plot is most representative of the thin-film intrinsic properties. As has been indicated in the introduction, one usually chooses the relative minimum that corresponds to $d/h$=0.1. The following phenomena were investigated to assess their influence on $E(d/h)$ and $H(d/h)$: substrate properties, pile-up and surface effects.

### 4.3 Influence of Substrate on Mechanical Properties

To assess the influence of the substrate on the measured thin-film mechanical properties, two substrates with contrasted mechanical properties have been used, namely soda-lime glass ($E$ = 72.5 GPa, $H$ = 5.4 GPa [17]) and silicon (Si(100): $E$ = 130.9 GPa; $H$ = 10.2 GPa [47]). The minimum hardness or elastic modulus shows no dependence on the particular substrate used: for a given binder and measured magnitude ($H$ or $E$) and within experimental error, all measured datapoints are lined up on a single curve (c.f. figure 4.4).

![Figure 4.4: Hardness and elastic modulus of thin-films on soda-lime glass and silicon.](image)

### 4.4 Elastic Modulus and Hardness: Interaction Film and Substrate

In figures 4.1a and 4.1b, B38 and B56 are characterised by, respectively: a smooth and an abrupt increase towards the $E$ and $H$ of the substrate. These transitions are related to the interaction within the thin-film between the indenter and the substrate. Larger stresses develop in B38 films creating a
'long'-range interaction compared to the 'short'-range interaction within B56 thin-films. Compared to the hardness, the elastic modulus is more strongly affected by the substrate, because the elastic field under the indenter is not confined to the film, but extends into the substrate [48]. The substrate stiffness is observed to influence the measured contact stiffness, thus elastic modulus. Consequently, for the elastic modulus there is a 'longer'-range interaction between the indenter and the substrate compared to the hardness.

4.5 Effect of Pile-up

As noted in chapter 2.3.4.2, a significant problem related to the Oliver-Pharr method is that the effect of material pile-up is not taken into account. To investigate the occurrence of pile-up in the two binders under consideration, indentations were performed to various depths within a thin-film. The residual imprint and the surrounding pile-up were then observed under an AFM, see figure 4.5.

![Figure 4.5: Examples of AFM scan (phase contrast) of residual imprint and surrounding pile-up after indentation. From left to right: Shallow to deep indentations in a B38 thin-film (50% solutions, spin-coated at 500 rpm).](image)

In figure 4.6 the pile-up height scaled to the indentation depth is plotted as a function of the indentation depth scaled to the film thickness for both B38 and B56. The error bars account for the measurement accuracy of the AFM pile-up profile. The pile-up height scales to the indentation depth up to an indentation depth equivalent to 20% of the B38 film thickness. An indentation depth equivalent to 20% of the film thickness represents therefore a critical depth for the B38 thin-film at which the plastic zone under the indenter starts to interact with the hard substrate [49]. Only two indentations were performed on B56 thin-films: the pile-up height scaled to the indentation depth showed no significant increase.

42
In figure 4.6, the pile-up height for B38 amounts approximately to 6.5% of the indentation depth. This will give an error in the contact area approximation of around 13% thus an error in hardness of around 13% and in elastic modulus of around 6.5%. As the indenter starts to interact with the substrate, the amount of pile-up increases significantly hence the error in hardness increases to an extremely high 56%. It can be seen that for indentation depths around 50% of the film thickness, B38 thin-films already show a large amount of pile-up whereas for B56 thin-films this increase in pile-up is not yet visible. For B56 thin-films there is a small increase in pile-up from 4 to 7% of the indentation depth. This difference between B38 and B56 is attributed to the asphaltene content of the binder. The more elastic asphaltenes are believed to push the maltenes from underneath the indenter towards the surface creating pile-up. Because the pile-up will increase as indentation depths increase, 'true' film properties cannot be measured at indentation depths near the interface with the substrate [48].

4.6 Effect of Surface: Indentation Size Effect

The initial decrease in hardness with increasing film thickness seen in figures 4.1b, 4.2b and 4.3b can be explained using the so-called mechanism-based strain gradient (MSG) plasticity theory [50], which applies for soft films on hard substrates. This theory states that the flow stress depends not only on the strain at a particular point (classical view), but also on the strain gradient at that point. This means that for shallow indentations, where \( d \ll h \), a significant increase in hardness due to strain gradient hardening is observed.

The strain gradient hardening effect for shallow indentations is also explained by Cheng and Cheng [46] who used equations for the force and contact area to examine the hardness at different indentation depths. They conclude that the hardness will reach a steady-state value when \( \bar{F} / P \) is kept constant and
that before this steady-state value is reached the hardness will decrease with increasing depth for a period which is a function of the material considered and the loading rate.

This phenomenon also applies when indenting bulk materials: at shallow indentations the indenter does not feel the influence of the hard substrate and a big strain gradient occurs when the indenter hits the material surface. As the indenter goes deeper into the material, the strain gradient becomes constant. However, for indentation depths almost equal to the film thickness, the indenter strongly senses the effect of the hard substrate and the increase in hardness is caused by hardening associated with the strong gradients of plastic strain in the film between the indenter and the substrate [51, 52]. As the indenter penetrates the substrate a significant increase in hardness is found due to the harder substrate.

We conclude that values measured at a $d/h$-0.1 are indeed characteristic of those of the thin film, in accordance with the general rule of thumb applied by many researchers stated in the introduction. In typical curves, the minimum values of $E(d/h)$ and $H(d/h)$ are usually encountered at $d/h$-0.1. These minimum values of $E$ and $H$ are considered here as most representative of the thin film properties.

4.7 Mechanical Properties of Binders

![Graph showing minimum elastic modulus and hardness versus film thickness](image)

**Figure 4.7:** Minimum elastic modulus and hardness versus film thickness. Asphaltene and maltene thin-films from B38 and B56 are designated as A38 and M38 and A56 and M56, respectively.

In figure 4.7 the minimum hardness $H_{\text{min}}$ and elastic modulus $E_{\text{min}}$ are plotted versus the film thickness for both the binder and its components. The overall trend is a decrease in both $H_{\text{min}}$ and $E_{\text{min}}$ with increasing thin-film thickness. (In figure 4.7 binders are coded as B, asphaltenes as A and maltenes as M)
Thin-films prepared from asphaltene show the weakest and those prepared from maltene the strongest (regardless of their B38/B56 binder origin) dependence of $H_{\text{min}}$ on film thickness. Considering $H_{\text{min}}$, B56 and maltene are comparable, whereas B38 is in transition between maltene and asphaltene. This supports the dominant role of maltene in the B56 and asphaltene in the B38 mechanical response.

Thin-films prepared from B38 can be fitted to a scaling law: $E_{\text{min}} \propto d^\alpha$. This does not apply for B56.

### 4.8 Comparison between mechanical properties of thin-films from spin-coated and melted binders

![Figure 4.8: Minimum elastic modulus and hardness versus film thickness for thin-films from spin-coated binders and melted binders, respectively.](image)

In figure 4.8, the minimum hardness $H_{\text{min}}$ and elastic modulus $E_{\text{min}}$ are plotted versus the film thickness for both the spin-coated binders and melted binders. The overall trend is a decrease in both $H_{\text{min}}$ and $E_{\text{min}}$ with increasing thin-film thickness. The preparation procedure does not influence the $H_{\text{min}}$ and $E_{\text{min}}$ measured on B38 but does significantly influence those measured on B56 thin-films. In the latter case, both the magnitude and trend are affected by changing the preparation procedure: $E_{\text{min}}$ and $H_{\text{min}}$ are higher for melted than spin-coated B56 thin-films.

### 4.9 Influence of Asphaltene Content on Mechanical Properties

Of interest is also whether the asphaltene content influences the mechanical properties of the binder. To determine the influence of asphaltene content on their mechanical properties, both considered binders were fractionated into their maltene and asphaltene components then recombined to match the asphaltene content of their counterpart. In this way, the asphaltene content in B38 and B56 binder originally amounting to 24.9w% and 12.6w% were brought to 12.6 w% and 24.9 w%, respectively. The recombined binders are designated as B38rec and B56rec, respectively.
In figures 4.9a and 4.9b, $E$ and $H$ are plotted for original and recombined binders. The hardness and elastic modulus of B38rec drop to the level of the hardness and elastic modulus of B56. As for B56rec, the hardness increases but fails to reproduce the B38 curve, whereas the elastic modulus remains that of B56. It appears that the high asphaltene content in B38 is a necessary condition for making it a stiff and hard material since halving the asphaltene content considerably reduces both the elastic modulus and hardness. However, it appears not to be a sufficient condition: other aspects of the material microstructure must also play a role.

In figure 4.10, AFM scans of the original and recombined binders are presented. It appears that the morphology changes upon recombination of a B38 (B56, respectively) binder with an amount of asphaltene matching its counterpart. For B38 thin-films, the clusters of asphaltene domains seen in the original binder seem to break-up into separate domains upon recombination. However, unlike in B56, the domains in recombined B38 are polydispersed with no increase in domain density with increasing film thickness. For B56 thin-films, the opposite happens and the domains seen in the original binder seem to form clusters. These clusters do not have the clear ‘flower’ pattern seen in B38 thin-films.
This suggests that asphaltene in both binders are in different colloidal state, which does not rely exclusively on the asphaltene content.

Figure 4.10: AFM scan (phase contrast) of original and recombined binders. B38 and B56 thin-films from a 5% solution and a spin-coating speed between 1000 and 4000 rpm can be seen.

4.10 Comparison of the Elastic Modulus of Thin-films and Storage Shear Modulus of Bulk Composite

The minimum elastic modulus measured by nanoindentation on B38 films is compared in figure 4.11 to the storage shear modulus (at high temperature/low frequency) of the same binder confined between mineral particles in a composite, as tested by Dynamic Mechanical Analysis (DMA) [15]. The elastic modulus $E$ versus film thickness of the thin-films and the storage shear modulus $G'$ versus filler concentration of the bulk composite are found to follow both a power law. In the composite material, this has been interpreted as the onset of a percolating network below a critical average interstitial gap between the mineral particles bridged by asphaltene aggregates. It is tempting to conclude, in light of Figure 4.11 that percolation also occurs in B38 thin-films. However, a more in-depth consideration is required, particularly on the equivalence between the two conformations—thin-film and composite—regarding dimension, geometry, time-temperature, and filler fraction versus film thickness.
However, it is worth mentioning the clear discrepancy between B38 and B56 in elastic modulus versus film-thickness. Whereas a power law applies for B38, B56 clearly shows a ‘collapse’ in modulus for films above a few μm thick, at which both films show complete coverage and comparable minimum moduli and hardnesses, that is a simultaneous similarity in both microstructures and mechanical properties.

**Figure 4.11**: Elastic modulus and storage shear modulus versus film thickness and interstitial gap between mineral particles.

### 4.11 Conclusions

In this chapter a better understanding of the mechanical properties of binders and their constituents is achieved. It has been confirmed that values of $E$ and $H$ measured at $d/h\sim0.1$ are characteristic for the thin-film. B56 shows mechanical properties similar to those of maltene, whereas B38 has mechanical properties intermediate between those of maltene and asphaltene. A comparison is made between a percolating bulk composite and the mechanical behaviour for a B38 binder thin-film.
Chapter 5

Lateral Force Apparatus

5.1 Introduction

In this chapter, results of friction force as a function of the sliding speed measurements are presented. Sliding scratch patterns are imaged using optical microscopy and AFM. The experiments presented here are again intended for a better understanding of the relationship between the binder morphology and composition, and its mechanical properties.

Experiments were carried out on thin-films made of B38 and B56 binder. Both binders were spin-coated onto glass substrates with a thickness of approximately 250 nm. The experiments followed a 'slide-hold-slide' procedure, as explained in chapter 2.4.2. The velocities used enclose the whole range of driving speeds available on the LFA, from 25 nm/s to 1 mm/s. An intermediate velocity of 10 μm/s was also used. The diameter of contact, \( D \), was determined with AFM.

5.2 Microscopy of scratches

In figure 5.1, an optical microscope image of scratches on B38 and B56 thin-films is shown at different scratch velocities. In figure 5.2, an optical microscope image of the slide-hold-slide pattern is shown.
Figure 5.1: Optical microscope image of scratches in B38 (left) and B56 (right) thin-films at different scratch velocities (scratch width ~10 μm).

Figure 5.2: Optical microscope image of slide-hold-slide pattern experiments. B38 (left) and B56 (right) thin-films at a sliding velocity of 1 mm/s. For B56, unlike B38 the hold period is visible.

On figure 5.2 no clear slide-hold-slide pattern is visible for scratches on B38. This means that during the hold period there was no additional radial outflow of binder compared to the outflow of material during sliding. Figure 5.1 shows that if the sliding velocity is lowered from 1 mm/s to 25 mm/s, dark spots appear along the edges of the scratch, which grow in size if the sliding velocity goes down.
For scratches on B56, at a sliding velocity of 1 mm/s the slide-hold-slide pattern can be distinguished, whereas for lower sliding velocities no such pattern could be seen. The black spots seen along the edges of the scratch on B38 are also present on B56. At the lowest sliding velocity (25 nm/s) ‘tongues’ sticking out into the scratch can be seen along the entire length of the scratch.

Next to optical microscopy, AFM was used to determine the effect of sliding velocity on the morphology of the scratch in a binder. From figure 5.3 there can be seen that the ‘tongues’ formed in scratches on B56 at the lowest sliding velocity are of the same height as the surrounding pile-up of material. The formation of these ‘tongues’ can be due to viscous-type behaviour of the B56 binder at a low sliding velocity, whereas for a high sliding velocity there is a more plastic-type behaviour. As the maltene fraction in B56 is higher than in B38, the viscous-type behaviour is more pronounced in B56, which can account for the formation of these ‘tongues’ on B56 and not on B38 scratches.

![Figure 5.3: AFM scan of scratch on B56 at a sliding velocity of 25 nm/s (topography).](image)

5.3 **Mechanical properties of scratches**

In figure 5.4 the diameter of contact between tip and sample is plotted as a function of the contact time, $D/v$, with $D$ the diameter of contact and $v$ the sliding velocity. The contact diameter grows in time due to creep for both the B38 and B56 thin-film. The growth in contact diameter is largest for the B38 thin-film.
Figure 5.4: Contact diameter $D$ versus contact time $D/v$.

The friction force, $F_{\text{friction}}$, is plotted in figure 5.5 versus the contact time, $D/v$. There can be seen that for B38 the friction force increases in time, whereas for B56 the friction force decreases in time.

Figure 5.5: Friction force versus $D/v$.

In other words, B38 shows velocity weakening: if the velocity is increased, hence the contact time decreased, the friction force decreases. This behaviour is generally creep controlled and observed in solids [53, 54]. B56 shows velocity strengthening. Although the contact area is growing in time due to creep (figure 5.3), the viscous behaviour dominates friction [54]. This behaviour can be explained by the fact that the maltene fraction is higher in B56 then in B38, which favours viscous-type behaviour. The network structure formed by asphaltene in a B38 binder can account for the solid-like behaviour of B38 observed in these measurements.
5.4 Conclusions

It can be concluded that the mechanical behaviour of the binders can be correlated to the composition of the binders. B38 shows a solid-like behaviour, whereas B56 shows a viscous-type behaviour. Not only the amount of asphaltene plays a role in the mechanical behaviour, also other differences in composition have an influence on the mechanical behaviour.
Chapter 6

General Conclusions

In this project the microstructure and micromechanics of C-fix binders and their constituents were investigated. The aim was to get more insight into the binder morphology in relation to its mechanical properties. The following conclusions can be drawn within that scope.

6.1 Microstructure

The microstructure of two C-fix binders (B38 with good properties for C-fix applications and B56 with bad properties for C-fix applications) confined as thin-films of adjustable thickness has been investigated, mainly using atomic force microscopy (AFM). Both binders, feature asphaltene domains surrounded by a smooth maltene phase observed at the thin-film surface. These asphaltene domains mainly differ in: mutual interaction, presumed adhesion to the substrate and wax growth. In relation to a higher asphaltene content in B38 than in B56, peptized by relatively less resins, asphaltenes are likely to have a higher surface energy. This may promote domain aggregation and adhesion to the substrate. Paraffin wax was only found on B38 binder thin-films in presence of maltene. On B56 binder thin-films, no paraffin wax was observed. On maltene thin-films, domains were still present. These domains are presumably formed by lower molecular weight —n-heptane soluble— asphaltenes and resins, still present in the maltene phase.

As the temperature is increased from room temperature to 120°C, thin-films prepared from the two binders behaved following what appeared as opposite patterns. In B38, the asphaltene domains decrease in size, whereas for B56, the asphaltene domains increase in size with increasing temperature. This reflects the difference in thermodynamical behaviour of the two binder colloidal states.

6.2 Micromechanics

The mechanical behaviour of C-fix binder thin-films has been characterised by nanoindentation. The asphaltene content was found to markedly influences the mechanical properties of the binder, yet not sufficiently to account for both qualitative and quantitative differences in mechanical properties.
between the two binders. As for the hardness and elastic modulus, B38 appears to be in transition between maltene and asphaltene, whereas B56 behaves almost like maltene. For B38, unlike B56, a scaling law is found for the elastic modulus versus film thickness, which may relate to similar observations on percolating C-fix composites.

The thin-film hardness can be described using the mechanism-based strain gradient (MSG) plasticity theory. ‘True’ film properties can be obtained at indentation depths around 10% of the film thickness, where the hardness and elastic modulus versus indentation depth have a minimum value. This is confirmed by measurements of pile-up height and of the influence of the substrate on the mechanical properties.

The scratch resistance of binder thin-films has been investigated using a lateral force apparatus (LFA). The influence of the sliding speed on the scratch morphology was observed by optical microscopy and AFM. In B56, unlike B38, ‘tongues’ are formed at a low sliding speed, which may pertain to the viscous behaviour of the B56 binder. B38 behaves as a more cohesive binder.

Friction force measurements showed opposite friction behaviour for B38 and B56. B38 showed velocity weakening, which is typically observed in solids, whereas B56 showed velocity strengthening, where friction is dominated by a viscous behaviour.

New insights have been gained into the microstructure and micromechanics of C-fix binders and their maltene and asphaltene fraction. The observation that C-fix binder produces composites with outstanding mechanical properties can now be understood in terms of more surface reactive (prone to network aggregation and association at surfaces and to provide a substrate for wax formation) asphaltene aggregates with a marked impact on the cohesive property and the mechanical behaviour, measured here at the nano-scale.
References


[54] R.P. Schaake, private communications
**Key to Symbols**

$A$ area [m$^2$]

$C$ capacitance [farad]

$D$ diameter of contact [m]

$E$ elastic modulus [Pa]

$E_r$ reduced modulus [Pa]

$F_f$ friction force [N]

$L'$ storage shear modulus [Pa]

$H$ hardness [Pa]

$K$ dielectric constant [-]

$P$ load [N]

$	ilde{P}$ load rate [N/s]

$Q$ current [A]

$S$ harmonic contact stiffness [N/m]

$V$ voltage [V]

$d$ distance/ filler size [m]

$e$ evaporation rate [m/s]

$f$ rotation speed [rpm]

$h$ film thickness [m]

$h_c$ contact depth [m]

$h_f$ final displacement after complete unloading [m]

$v$ velocity [m/s]

$z$ normal displacement [m]

$\Lambda$ inter-particle distance [m]

$\varepsilon_0$ permittivity of free space [farad/m]

$\phi$ filler fraction [-]

$\phi_c$ critical filler fraction [-]

$\phi_{\text{max}}$ maximum filler fraction [-]

$v_0$ initial viscosity [m$^2$/s]

$\rho$ density [g/cm$^3$]
Acknowledgements

First of all I would like to thank my supervisors:

Erwan Sourty, as my supervisor and colleague, you were great to work with.

Willem-Pier Vellinga, your enthusiasm reflected on both me and Erwan, and helped us to obtain good results throughout the whole project.

Prof. Michels, during our fruitful discussions, your knowledge and expertise have helped the project a lot.

Also I would like to thank my roommates and all the students of Dispuut 3004 with whom I shared many coffeebreaks and lunches.

And last, but not least, I would like to thank all people that helped me the past year: the whole polymer physics group, prof. Meijer, Richard Schaaake, Christophe Pelletier, Marc van Maris, Toon Hoeben, Henk Janssen, Pit Teunissen and many others in the mechanical engineering and chemistry departments.