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## **Turning Back Time: Rheological and Microstructural Assessment of Rejuvenated Bitumen**

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**ABSTRACT**

Countermeasures to the ageing of bituminous asphalt binders is a highly important topic, both for service-life extension of asphalt ‘in the field’ and for recycling old pavements (RAP) into new structures with similar functional requirements as the original structure. Usually this is achieved by applying additives that restore the adhesive and mechanical properties of the original bituminous binder. These additives are commonly termed (asphalt) rejuvenators. Here we examine the performance of two very distinct rejuvenating agents. Usually the effectiveness of rejuvenators is measured by comparing the penetration and softening point of the rejuvenator-aged bitumen blend to reference values of the virgin binder. First, the rejuvenating capabilities of the two additives are evaluated in terms of rheology using a dynamic shear rheometer. Then the microstructures of the virgin binder and the rejuvenated blends are obtained by means of atomic force microscopy. Subsequently the rheological results are related to the microstructure morphologies.

One finds from rheology that both rejuvenators exhibit the desired softening and property restoring performance. Though, one rejuvenator does so at much lower dose rates. By correlating rheology to the microstructural observations one finds that the effect of both rejuvenators is very distinct at microscopic length scales: rejuvenation is achieved by distinct chemo-physical mechanisms. One of the rejuvenators restores the virgin microstructure, whereas the other rejuvenator generates a new morphology.

Thus, it is demonstrated that by combining rheological and microstructural techniques, the mechanism and performance of rejuvenation can be understood. This may guide future designs and optimization of asphalt rejuvenating agents.

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## INTRODUCTION

Ageing of asphalt pavements is like a doubly edged sword of Damocles: it leads to premature failure of pavements due to ageing related embrittlement of the bituminous binder. At the same time the material cannot be recycled by just milling of the old pavement, reheating and laying it. The reason for this is the irreversible nature of the chemical reactions that cause ageing; mainly oxidative and UV-radiation induced chemical cross-linking.

To deal with the undesirable effects of the ageing of pavement materials 3 types of strategies may be adopted (1): preventive treatments of the pavement with anti-ageing agents, corrective treatments like repairs of cracks by sealants and reconstructive treatments (recycling or replacing). Because of ever increasing demands with respect to sustainable use of raw materials and optimal availability of infrastructure, all three strategies are incorporated on equal footing in life cycle based construction, maintenance and replacement decision models. Remarkably, the engineering solution to the three treatments is rather similar, though different terms are adopted by the industries that specialize in either of the aforementioned strategies.

In the industry of preventive and corrective pavement treatments terms like ‘service life extender’, ‘softening agents’(2; 3) and ‘rejuvenator seals’(1) are commonly used, whereas in the recycling business terms likes ‘recycling agents’, ‘recycling additives’, ‘rejuvenating agents’ or simply ‘rejuvenator’ are frequently used. But, notwithstanding all these different terms, all these products act on the asphalt binder as a softening agent that ideally also promotes or restores the binder’s adhesive properties. This is achieved by replenishing the volatiles and light bitumen fractions that have been lost during laying and subsequent ageing of the pavement. Many authors (4; 5) explain the treatment strategy as restoration of the asphaltene-maltene ratio, the level of the virgin bituminous binder. In the remainder all these products will be termed as rejuvenators.

Because of the demand for low price, availability and recycling reasons, rejuvenators are usually waste products. Many different types have been reported: refined tallow, waste vegetable oil, waste frying oils, soft bitumen, (paraffinic) base oils, waste motor oils, ‘engineered’ products, emulsions, tertiary amines etc. (6-8) . The main difference is in the way that these materials are being applied in practice and their application temperature, i.e. hot or cold (11;12). Preventive treatments (e.g. spraying on roads) require a design of the additive that promotes rapid diffusion through the top layer of the asphalt, while pre-emptive treatments require some sort of encapsulation of the rejuvenator (9). In the remainder emphasis will be on rejuvenation of the aged bitumen in recycled asphalt pavement (RAP).

Probably over 90% of the total RAP in The Netherlands is being reused in new asphalt constructions. This recycling practice started with the oil crisis in 1973 and the invention of the milling machine at that time (10). Typically, RAP from surface layers contains high quality aggregates coated with very hard bitumen, which is normally recycled into base layers. It is not allowed to recycle the RAP from derived from surface layers again into surface layers because of uncertainty about performance and durability of the recycled porous asphalt. As a result, restoring the intrinsic properties of recycled porous asphalt during recycling process is of great interest for surface-to-surface recycling.

Thus the challenge is to recover properties such as modulus and strength level of the unaged bitumen (11). Therefore the effect of two very distinct rejuvenators is considered in this study. Firstly by means of assessing the rheology (usually pen and softening studies are reported), and then relating this to the more fundamental property of bitumen structure at the micrometer length scale (6; 12-16), which can be assessed by means of atomic force microscopy (AFM).

## MATERIALS & METHODS

### Preparation and Mixing of Bituminous Binders and Rejuvenators

Virgin, straight run bitumen with a penetration grade of 70/100 was obtained from the Q8 Petroleum Company. In order to consistently mimic a RAP binder, a batch of the same material was aged in an accelerated manner by means of the rotational cylinder ageing tester, RCAT (17). The laboratory aged bitumen (P1) was produced by pouring 500 grams of the virgin bitumen into the RCAT cylinder and subsequent rotating it at a rate of 5 rotations per minute for 18 hours at an ageing temperature of 163 °C.

The two distinct rejuvenators selected for this study were provided by Latexfalt BV: an emulsion type rejuvenator (BM1), which visually resembles bituminous emulsions, and a liquid type rejuvenator (CM1). The laboratory aged bitumen and the rejuvenator were then mixed for 15 minutes at 150 °C. In this way three batches of mixes were produced: the aged binder P1 with 20% rejuvenator BM1 assigned P1BM1\_20, and the same aged bitumen mixed with 10% and 25% rejuvenator CM1 respectively (P1CM1\_10 and P1CM1\_25). These mixing ratios were selected according to the logarithmic blending rule (18) as given in Equation 1:

$$\log(|G^*|_{mix}) = a \log(|G^*|_{P1}) + b \log(|G^*|_{Rejuv.}) + abG_{P1-Rejuv.} \quad (1)$$

with

$|G^*|_{mix}$  the complex shear modulus of the rejuvenator-aged bitumen blend [Pa],

$|G^*|_{P1}, |G^*|_{Rejuv.}$  the complex shear moduli of P1 and the rejuvenator [Pa],

$G_{P1-Rejuv.}$  interaction term accounting for non-ideal mixing between rejuvenator and aged bitumen, and  $a, b$  the fractions of aged bitumen and rejuvenator in the mix ( $a + b = 1$ ).

According to this rule the rheological properties of the virgin 70/100 bitumen would be restored by respectively adding 20% of the rejuvenator BM1, or 10% of the rejuvenator CM1, to the aged bitumen P1. It should be noted that the mass fraction of the emulsion type rejuvenator BM1 is based on the residual mass, i.e. after evaporation of the water. For studying the influence of the dosage of CM1, one mix containing 25% CM1 (P1CM1\_25) was prepared. Table 1 summarizes the materials used in the present study.

**TABLE 1 Material Properties (Penetration @ 25 °C in 1/10 mm Units According to EN1426:2000)**

	Virgin 70/100	P1	P1BM1_20	P1CM1_10	P1CM1_25	BM1	CM1
<b>materials</b>	Virgin bitumen (83 pen.)	Lab aged bitumen (25 pen.)	20 mass% BM1 (residual) blended with P1	10 mass% CM1 blended with P1	25 mass% CM1 mixed with P1	emulsion type rejuvenator (evaluation on residual)	liquid type rejuvenator
<b>viscosity at 60 °C [Pa·s]</b>	242.2	1067.9	305.7	110.4	22.8	5.0	0.2

### AFM Sample Preparation, Instrumental Settings and Measuring Environment

Steel sample disks with a diameter of 12 mm were used as sample substrates for the AFM measurements. The specimens were prepared by applying 30 mg of binder sample to the substrate with a spatula and subsequent heating on a hot plate of 100 °C for 30 seconds, in order to create a thin (0.3-0.5 mm), flat film. Then the specimens were thermally conditioned inside an oven at 100 °C for 30 minutes followed by cooling in ambient air and equilibration at room temperature for 24 hours (14; 19). For all materials in Table 1 specimens were prepared according to this procedure, except for the pure rejuvenators BM1 and CM1. The latter two samples would be too soft to be imaged with the selected AFM settings.

For this study the Multimode V Atomic Force Microscope from Bruker (Santa Barbara, USA) was used in tapping mode and in air at ambient temperatures (22 °C). The probe scan rate was chosen to be 1.0 Hz (1 line/s) and overview scans of the microstructure of the various samples were recorded at 30×30 μm<sup>2</sup> scan size with a pixel resolution of 512×512. Details of the microstructure were obtained at scan sizes of 10×10 μm<sup>2</sup> and 3×3 μm<sup>2</sup> with similar scan rates and pixel resolutions as before.

Commercially available high resolution tapping mode silicon cantilevers RTESPA (Bruker) were used. These cantilevers have a nominal resonant frequency of 330 kHz and a nominal force constant of 40 N/m. The cantilever material is Antimony (n) doped Silicon which has 40±10 nm aluminum reflective coating on its backside. The reflective coating helps to increase the intensity of the reflected laser signal and it protects the bitumen sample from softening by laser exposure. The nominal cantilever dimensions were 120×35×3 μm<sup>3</sup>. The cantilever has a chemically etched rotated silicon tip on its edge to provide a more symmetric representation of features over 200 nm in height. The tip height is in the range of 15-20 μm and it has nominal tip radius of 8 nm. The Gwyddion software package (20) was used to correct for non-flatness of the sample surface and to conduct quantitative image analysis.

## EXPERIMENTAL RESULTS AND DISCUSSION

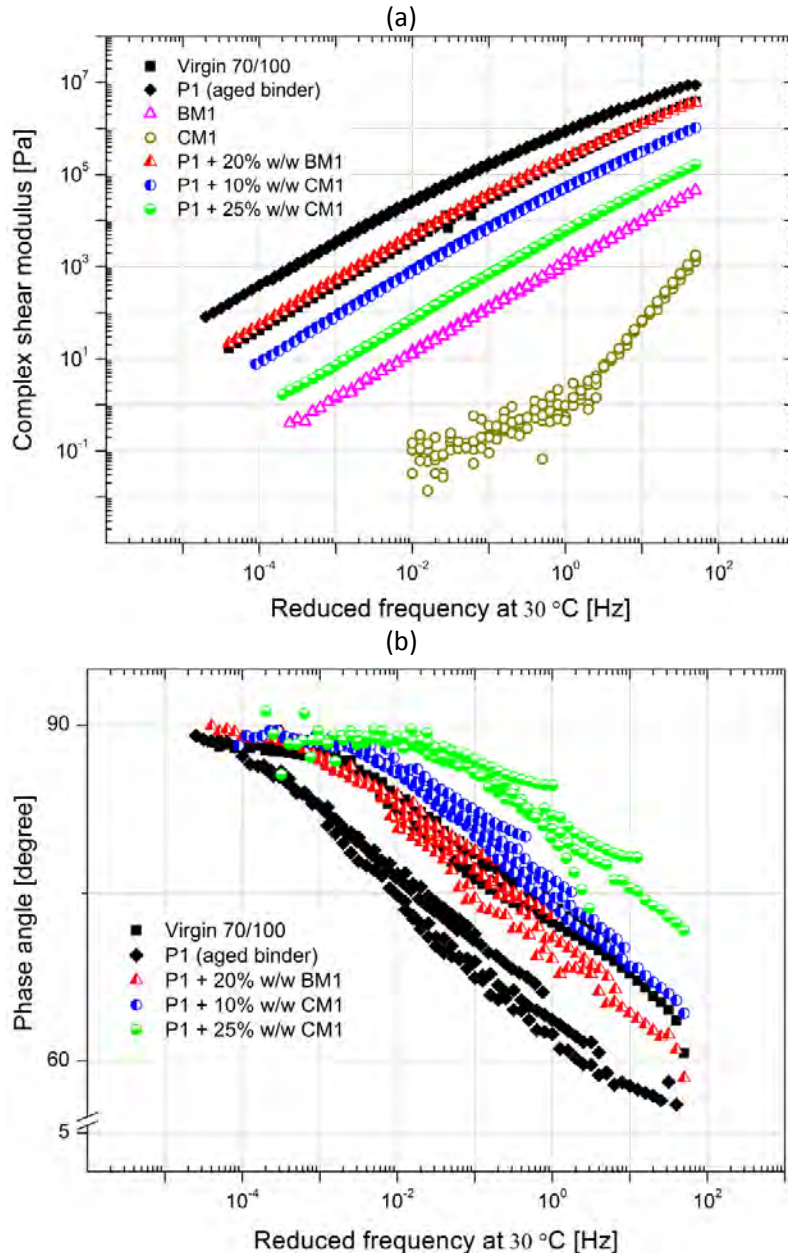
### Rheology of the Binders, Rejuvenators and their Blends

Figure 1 shows the results of the rheological properties of the laboratory aged bitumen, rejuvenators and their blends. The rheological measurements were conducted at 30, 40, 50 and 60 °C using a Dynamic Shear Rheometer (AR 2000ex rheometer from TA Instruments), and the results were shifted to a reference temperature of 30°C using the time-temperature superposition principle.

Firstly one observes that the laboratory aged bitumen P1 shows higher complex shear modulus and lower phase angle compared to the virgin 70/100 bitumen, as could be expected. On ageing the bitumen becomes stiffer (Figure 1a) and less viscous (Figure 1b). The neat rejuvenators show very distinct behaviour. The rheology of the emulsion type rejuvenator BM1 behaves as low viscosity bitumen, while the liquid type rejuvenator CM1 has very distinct rheological characteristics. Firstly, it displays a much lower, almost frequency independent, shear modulus at low frequencies. At a frequency of about 3-5 Hz an abrupt increase in shear modulus is observed, a signature of dilatant or shear thickening response. This might be caused by the presence of suspended particle like structures in rejuvenator CM1 or the formation of such structures at higher shear rates.

The addition of rejuvenator BM1 into the aged bitumen decreases the complex shear modulus, while the phase angle does increase to the level of the virgin bitumen. The prediction of Equation 1 for the required mass fraction of 10% rejuvenator BM1 to restore the rheological properties of the aged binder to the level of the virgin binder is almost perfect, as the curves of P1BM1\_20 and the curve of the virgin binder almost completely overlap. It can also be observed that the CM1 is more efficient than the

5 BM1 rejuvenator in re-establishing the rheological properties, as a lower concentration (10%) of this rejuvenator already softens the aged binder to values below those of the virgin bitumen (overshoot). The higher concentration of 25% of rejuvenator leads to even lower values of the shear modulus of the mix. It should be noted that in a blend with aged bitumen, any signature of the dilatant nature of the pure rejuvenator CM1 is completely lost. Blends of rejuvenator CM1 with aged bitumen possess master curves that are similar (parallel) to virgin or aged binders as well as aged binders rejuvenated with BM1.



**FIGURE 1 (a) Complex shear modulus and (b) phase angle master curves of virgin and laboratory aged bitumen, rejuvenators and their blends at a reference temperature of 30 °C.**

Thus, for the rheological frequency range studied, the effect of adding rejuvenator CM1 is comparable to that of addition of rejuvenator BM1, however a similar softening effect is achieved at lower additive doses of CM1. This is also found by exploiting equation 1. The interaction parameter  $G_{P1-Rejuv.}$  is calculated for BM1-aged bitumen,  $G_{P1-BM1} \sim -1$ , and for the CM1-aged bitumen system,  $G_{P1-CM1} \sim -8$ . Thus, the interaction parameter of CM1 is almost an order of magnitude larger than for the case of BM1. From this, the minimum dosage for restoring the rheological properties of CM1-P1 system was found to be about 5%, which is indeed less than the amount of 10 mass % BM1 rejuvenator required to achieve the same. Finally, addition of rejuvenator CM1 leads to pure viscous response (phase angle of 90 degrees) up to frequencies of 0.1 Hz, whereas the response of the virgin, aged and BM1 rejuvenated bitumen is only fully viscous for frequencies from 0.0001-0.001 Hz.

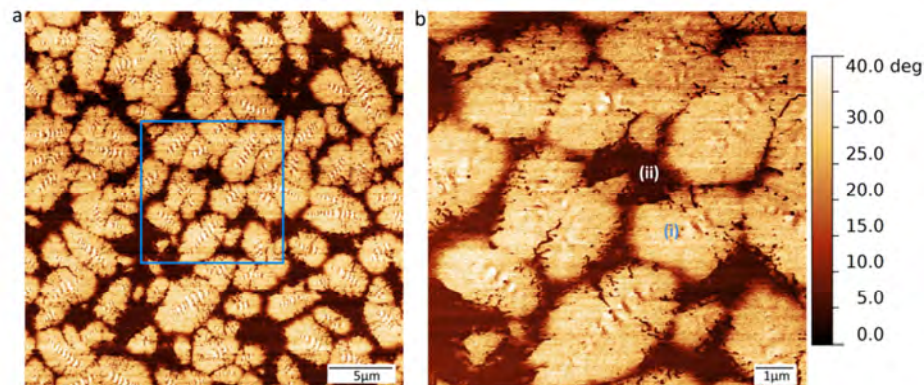
### Microstructure of Binders and Rejuvenated Binders from Atomic Force Microscopy

The microstructure morphology of the thin film bituminous surface was characterized by tapping mode AFM for samples prepared according to the procedure described before. In the context of this research the two main output channels, measured simultaneously, are used: i) height images which disclose the surface topography of the bitumen surface, and ii) phase images which provide a qualitative contrast in local mechanical properties of the surface, revealing the heterogeneity of the local material composition. The scan speed (1.0 Hz) over the surface was found to be adequate to resolve all features of interest.

### Microstructure of the Virgin Binder

The phase images of the virgin binder are very comparable to observations of bitumen with a similar pen grade as reported elsewhere (6; 19). Figure 2 shows that the virgin bitumen is essentially a two phase material. One microstructural phase, indicated with (i) in Figure 2b, consists of smooth, elliptical domains (domain or bee phase). This phase is dispersed in a continuous or matrix phase, (ii) in Figure 2b. Both phases have distinct material properties, which introduces a phase shift in the tapping response. This phase shift can be associated with a (mechanical) contrast between the phases. This leads to the appearance of lighter (elliptic domains) and darker (matrix) regions, as can be verified from Figure 2.

The topography images see Figure 8a, show that the elliptical domains display height undulations, 'wrinkling', in the middle of the domain along its long axis. The lengths of the domain long axes are found to vary between 2 and 6  $\mu\text{m}$ . Finally it is found that the domains are buried about 2-5 nm with respect to the average height of the continuous phase.



**FIGURE 2** Microstructure of virgin PEN 70/100 bitumen: (a) 30x30  $\mu\text{m}^2$  AFM phase image, (b) 10x10  $\mu\text{m}^2$  detail with (i) an elliptical domain, and (ii) the matrix phase.

### Microstructure of the Laboratory Aged Binder

The microstructure of the lab aged binder (P1), Figure 3, differs significantly from the virgin bitumen. Three separate microstructural phases are observed from the AFM phase images, Figure 3: a phase consisting of elliptical domains, Figure 3b(i), dispersed through a matrix with a lower phase shift, Figure 3b(ii). Finally, a hitherto never observed tertiary phase is observed, which consists of fine dark arcs and spots dispersed throughout the matrix, Figure 3b(iii). This tertiary phase displays the lowest phase shift, and it is the softest phase. It is speculated that the tertiary phase is an oxidation product in P1 without chemo-physical affinity with the other phases, which has formed regions of high liquidity. Its precise composition and impact on the bitumen performance will be subject to future research.

The elliptical domains have a broad size distribution, ranging from 0.8  $\mu\text{m}$  to 5  $\mu\text{m}$ . Also much smaller features (40-70 nm) composed of the same – elliptical domain – phase are found dispersed throughout the matrix. Therefore they are termed ‘debris’ from here onwards. As before, the elliptical domains display a wrinkling pattern along their long axes. Moreover, the phase boundary between the domains and the matrix is found to be less smooth than for the virgin binder.

From the topography image, Figure 8b, it is found that the elliptical domains are on average 5-8 nm lower (buried) in the matrix, while the tertiary phase protrudes above the matrix phase by 3-5 nm.

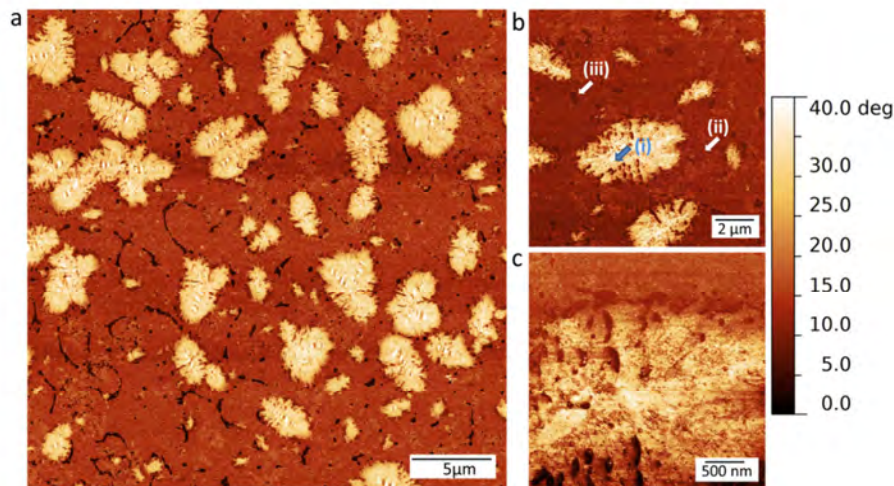
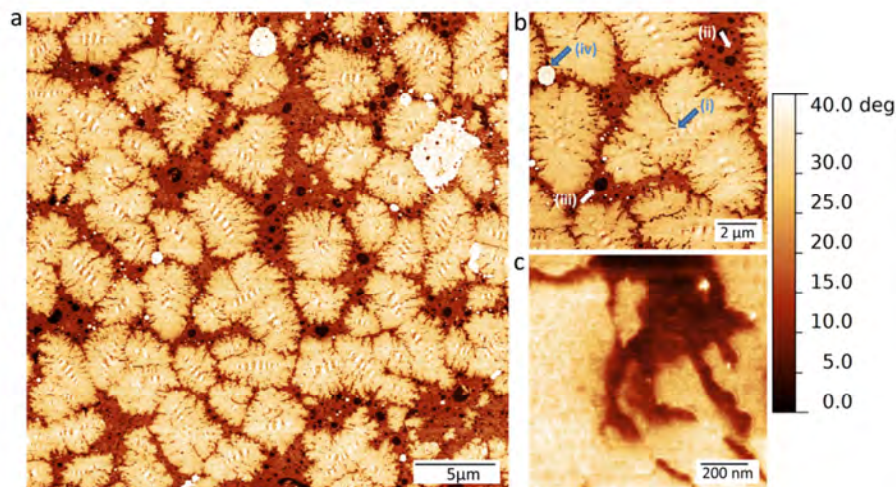


FIGURE 3 Microstructure of lab aged binder: (a)  $30 \times 30 \mu\text{m}^2$  AFM phase image, (b)  $10 \times 10 \mu\text{m}^2$  detail, with (i) elliptical domain, (ii) matrix, and (iii) tertiary phase, and (c)  $3 \times 3 \mu\text{m}^2$  detail.

### Microstructure of the Aged Binder Blended with Rejuvenator BM1

The microstructure of aged binder P1 blended with 20% BM1 rejuvenator, Figure 4, resembles closely the global features of the virgin binder’s microstructure (cf. figures 2 and 4), i.e. the sharp phase separated bitumen are restored by adding this rejuvenator grade. This is in agreement with the rheological results, where the shear moduli of the virgin and 20% BM1 rejuvenated binder almost completely coincide.



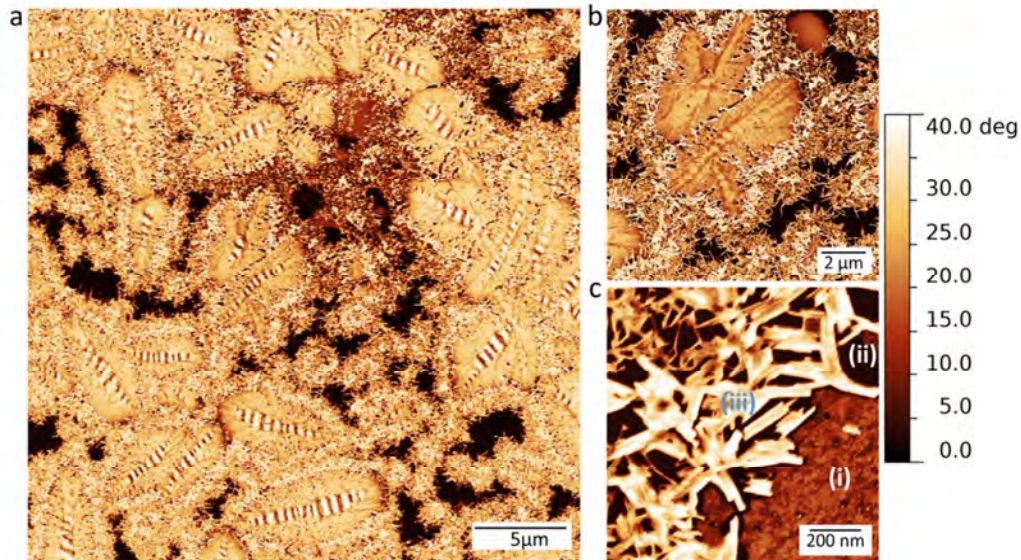
**FIGURE 4** Microstructure of aged binder blended with 20% w/w rejuvenator BM1: (a)  $30 \times 30 \mu\text{m}^2$  phase image, (b)  $10 \times 10 \mu\text{m}^2$  detail with, (i) elliptical domain, (ii) matrix, (iii) tertiary phase, (iv) quaternary phase. (c) High resolution  $1 \times 1 \mu\text{m}^2$  detail revealing dendritic pattern at phase boundary.

Despite its resemblance with the virgin binder, now four different phases can be distinguished. Firstly, the elliptical domains, Figure 4b(i), constitute the dominant phase. The high resolution AFM image of Figure 4c shows that the domain boundary now displays a dendritic pattern. The domains are again dispersed throughout the matrix phase, Figure 4b(ii). A tertiary phase, resembling the one in the aged binder, comes along in circular shape dispersed throughout the matrix phase, Figure 4b(iii). Lastly, a new quaternary phase is found (only visible from the phase image) to exist at the boundary of the domains and at the interstitial spaces of consecutive domains, Figure 4b(iv). This new phase has the highest phase shift (and is the stiffest phase), and it appears in almost circular shape with sizes between 200 nm and 4  $\mu\text{m}$ .

The size of the elliptical domains ranges from 2.2  $\mu\text{m}$  to 6.7  $\mu\text{m}$  and the typical wrinkling pattern along the long axis is also observed. In this binder-rejuvenator blend very few domain debris are found in the size range of 40 to 90 nm. Again, the elliptical domains are on average 3-8 nm lower in height than the matrix. The same holds for the new quaternary phase. The tertiary phase again rises 2-5 nm above the average matrix surface height.

#### **Microstructure of the Aged Binder Blended with 10% Rejuvenator CM1**

The microstructure of aged binder P1 blended with 10% CM1 rejuvenator, Figure 5, shows a completely new microstructural morphology. The elliptical domains are still present as well as the continuous matrix phase. But at the addition of rejuvenator CM1 a new phase of needle-like particles appears. These needles have a width ranging from 20 to 90 nm, and lengths between 50 and 250 nm. Closer inspection reveals that these needles are themselves structured: they are composed of (nano-) filaments with a diameter (width) of 2 to 5 nm and lengths of 20 to 70 nm. The high-resolution AFM image (Figure 5c) shows that singular filaments also occur, though their more stable conformation appears to be as a building block of the observed needle-shaped structures.



**FIGURE 5** Microstructure of aged binder blended with 10% rejuvenator CM1: (a)  $30 \times 30 \mu\text{m}^2$  AFM phase image, (b)  $10 \times 10 \mu\text{m}^2$  detail, (c) high resolution  $1 \times 1 \mu\text{m}^2$  detail with (i) elliptical domain, (ii) matrix phase and, (iii) needles forming a network phase around the domain phase. The very thin needles in (c) are the (nano-) filaments.

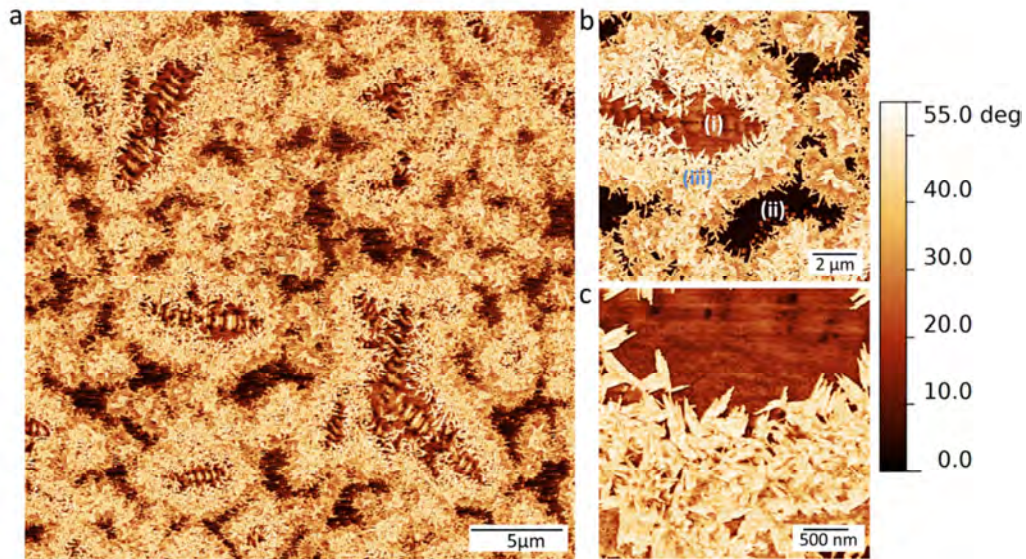
By analysing and comparing the topological profiles between isolated filaments and the needle structures, one finds that needles consist of bundles of 2 to 3 filaments. The needles form a mikado-like network structure, which forms a 1-2  $\mu\text{m}$  interface layer between the elliptical domains and the matrix. The colour gradient of this network phase (Figure 5) indicates that the needles get more densely packed towards the elliptical domains, where it is the stiffest component of the structure. This observed network phase very much resembles actin filament networks (21), the key structural and mechanical components of cells. This may hint towards a biological origin of the CM1 rejuvenator.

The size of the elliptical domains ranges from 2.2  $\mu\text{m}$  to 8.7  $\mu\text{m}$  and from AFM height images it is found that the average height of this phase is 5-8 nm lower than the matrix, whereas the network phase is on average 4 nm lower than the domains. The larger domains exhibit wrinkling pattern.

Compared to the microstructure of the aged bitumen, the addition of rejuvenator CM1 seems to replenish the elliptical domain phase, meanwhile softening the aged binder. This suggests that CM1 acts as a lubricant between the original bituminous phases. As was found in the rheology experiment (Figure 1), addition of 10% CM1 softens the aged binder below the level of the virgin binder. It is speculated here that the thickness of the network interface layer may control the amount of softening.

#### Microstructure of the Aged Binder Blended with 25% Rejuvenator CM1

Addition of 25% rejuvenator CM1 leads to a similar microstructure as observed for the P1CM1\_25 blend, Figure 6. The typical elliptical domains and matrix phases and the network phase in between, is also observed for this dose of CM1 rejuvenator. However, the increase of concentration of CM1 has contributed to the growth of the thickness of the network phase in between the matrix and elliptical domains to 3-3.5  $\mu\text{m}$ , mostly at the expense of the elliptical domains. At this concentration, the network is the most prominent phase present at microstructural level.

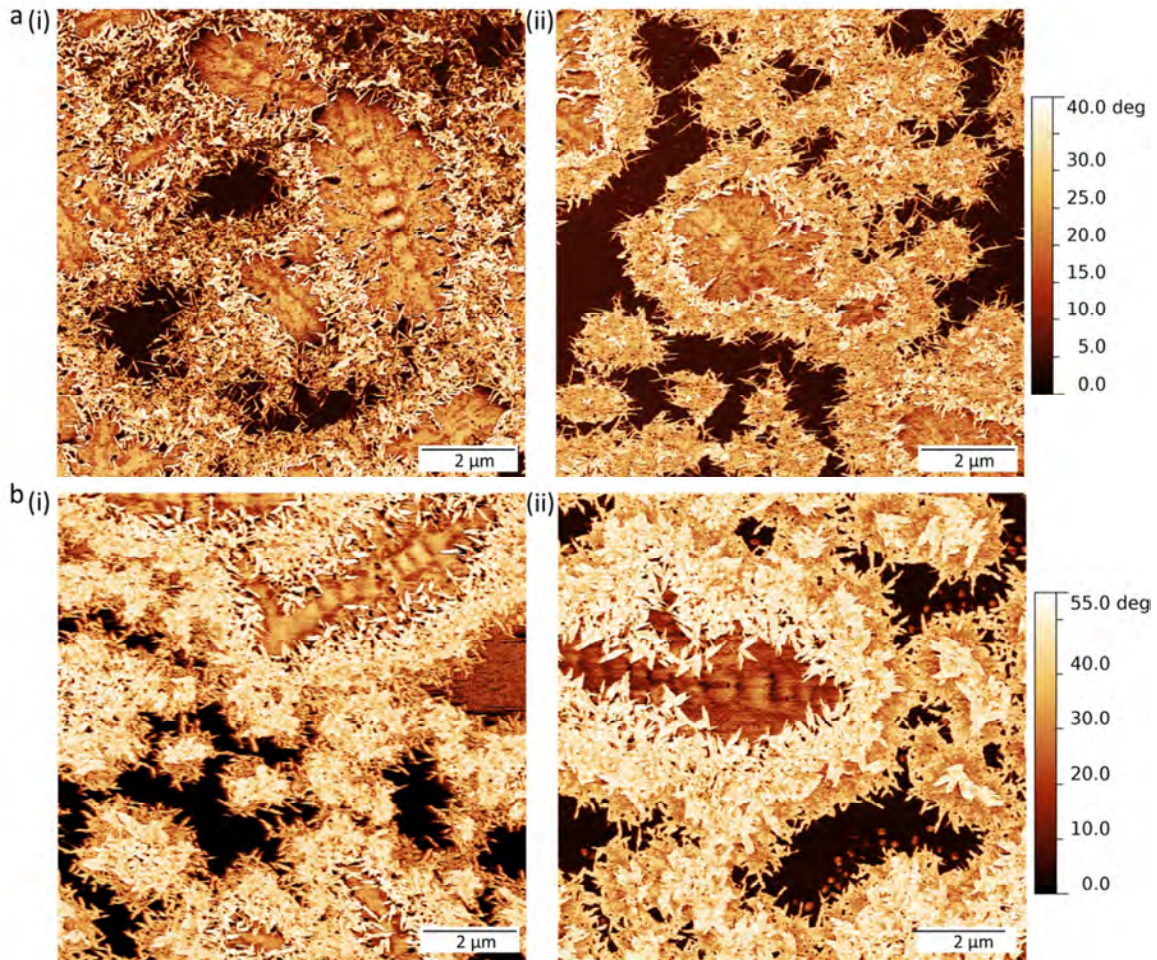


5 **FIGURE 6 Microstructure of aged binder blended with 25% rejuvenator CM1: (a)  $30 \times 30 \mu\text{m}^2$  AFM phase image, (b)  $10 \times 10 \mu\text{m}^2$  detail, with (i) domain phase, (ii) matrix, (iii) network phase, and (c) high resolution  $3 \times 3 \mu\text{m}^2$  detail.**

10 The sizes of the elliptical domains range from  $2.4 \mu\text{m}$  to  $10 \mu\text{m}$  and the wrinkling in the middle is still present. Finally, analysis of the height image (Figure 8) shows similar trends of the average topological heights of the distinct phases: the network phase is buried 3 nm relative to the average height of the domains, whereas these are about 10 nm lower than the matrix. The relative topological heights of the phases are consistent for the (aged) bitumen and the blends with rejuvenator additives, which suggests that the height difference is an inherent chemo-physical interaction property between the phases.

### 15 **Temporal Microstructural Development of the CM1 Rejuvenated Binder**

After 7 days of storage, all rejuvenated samples were reassessed to check whether the microstructure of the rejuvenated system evolves over time. The neat aged binder and the aged binder rejuvenated with 20% BM1 rejuvenator did not display any change over time. However, the aged binder rejuvenated with both 10% and 25% CM1 rejuvenator shows evolution of the microstructure over time (Figure 7).



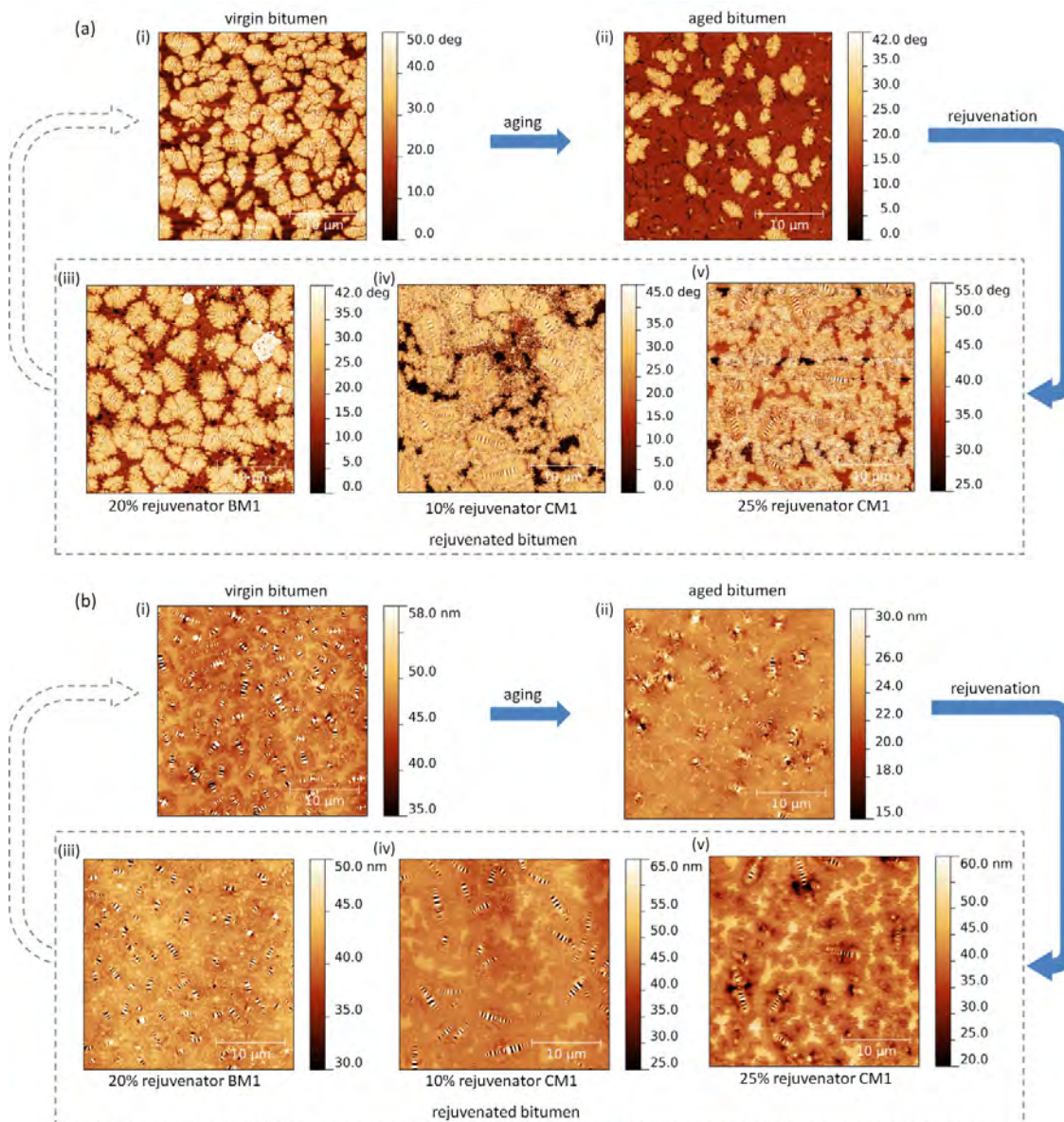
**FIGURE 7** Temporal change of microstructure of aged binder blended with CM1.  $10 \times 10 \mu\text{m}^2$  AFM phase images: (a) 10% CM1 and b) 25% CM1, (i) after preparation (ii) after 7 days.

5 The most profound temporal change is observed for the blend with the lower (10%) concentration of CM1 rejuvenator (Figure 7a). Over time needles are expelled from the matrix phase, disconnected domains only comprising the network phase are borne, and the amount of wrinkling in the elliptical domains tends to decrease (more images are available, and this is representative). The network phase has formed a kind of bilayer around the elliptical domains, consisting of 200-300 nm stiffer layer (higher phase shift, light colour in Figure 7bii), surrounded by a 1 μm somewhat softer layer. Both layers display the typical pattern of randomly oriented needles, typical of the network phase. The higher stiffness layer may be just a denser packed region of the network phase.

10 For the higher concentration of 25% CM1 rejuvenator the temporal change of microstructure is less pronounced. Islands solely consisting of the needle network are visible, as well as the bilayer of needles surrounding the elliptical domains. It is remarkable that here the stiffer (white) region of the needle network phase is the more prominent phase. Also at a 25% concentration of CM1, the wrinkling in the elliptical domains remains present over time, though the oscillation amplitude has decreased.

### Summary of Results

The effect on the microstructure of ageing and subsequent rejuvenation with two distinct rejuvenating agents is summarized in Figure 8. Here both the height and phase representation of the various microstructures are presented, demonstrating that rejuvenation of aged asphalt binder happens through interventions at the microstructural length scale. From rheology it is shown that both rejuvenators possess the capability of softening the aged bitumen, though through very distinct interventions at the microstructural level, Figure 8.



10 **FIGURE 8**  $30 \times 30 \mu\text{m}^2$  AFM (a) phase and (b) topography images, showing the microstructural effects of ageing and subsequent addition of the BM1 and CM1 rejuvenators.

The most important observations of the microstructural morphology of the neat and rejuvenated binders are summarized in Table 2.

**TABLE 2 Qualitative Microstructural Properties of Neat, Aged and Rejuvenated Binders**

<b>Microstructural feature</b>	<b>Aged binders (virgin<sup>*</sup>)</b>	<b>P1 + 20% w/w BM1</b>	<b>P1 + 10% w/w CM1</b>	<b>P1 + 25% w/w CM1</b>
<i>No. phases observed</i>	3 (2)	4	3	3
<i>Dominant phase</i>	matrix (domains)	elliptical domain	elliptical domain	(needle) network phase
<i>Appearance domain phase</i>	isolated domains (isolated domains)	domains well dispersed, some clustering	domains surrounded by network phase	domains surrounded by the network phase
<i>Wrinkling (domains)</i>	Present (present)	present	present	present
<i>Domain debris</i>	Present (-)	present	-	-
<i>Tertiary phase</i>	circular and arc shaped features in matrix (-)	circular shaped phase with a large size distribution	network of needles	network of needles
<i>Quaternary phase</i>	- (-)	stiff, circular features dispersed in matrix	-	-
<i>Microstructure recovery upon rejuvenation</i>	-	close to the virgin microstructure	larger domains than the virgin material, interfacial network phase	larger domains than the virgin material, interfacial network phase dominant

5 <sup>\*</sup>Virgin binder properties given in brackets.

## CONCLUSIONS

10 The effect of two distinct rejuvenators on the rheology and microstructure of laboratory aged bitumen has been studied. One of the rejuvenators (BM1) was of the emulsion type, while the other (CM1) was a liquid type rejuvenator. The difference between the two rejuvenator types was also evidenced by rheological data obtained with a DSR: the emulsion type rejuvenator's rheology resembled that of a very low viscosity bituminous binder, whereas the liquid type rejuvenator displayed an even lower viscosity together with a very strong rise of the master curve at a frequency of 0.2-0.5 Hz, which can be attributed to shear thickening of this rejuvenator type.

15 As expected, and reported throughout in literature (2; 3; 5; 8; 22), upon ageing the master curve shifts towards higher complex modulus values. Upon addition of rejuvenators the master curve of the blend is found to shift back to lower values, as intended and expected. Thus, from the DSR data it is

evident that the mechanical properties of the blend are in between those of the non-blended constituting components of the blend. Actually, for the probed frequency range addition of 20% of rejuvenator BM1 leads to a perfect overlap with the master curve of the virgin bitumen, i.e. complete rejuvenation of the aged binder.

5 Addition of rejuvenator CM1 to the aged binder displays a similar rheological effect, a down-shift of the master curve. Any signature of shear thickening as observed for the pure CM1 rejuvenator is absent in the blend: the master curve behaves as that of a regular bitumen. Moreover, blending of 10% of CM1 to the aged bitumen leads already to a softer blend than addition of 20% BM1. From a rheological point of view CM1 is the more efficient rejuvenator. From rheology it follows that complete  
10 rejuvenation of the aged binder by CM1 will happen at doses smaller than 10 mass percent.

For the same materials the microstructure morphology was experimentally determined by means of tapping mode atomic force microscopy. From the microstructural point of view rejuvenation would require the reappearance of the microstructure of the virgin binder upon addition and mixing of the rejuvenation agent.

15 Firstly the microstructures of the virgin and aged bitumen were determined. The effect of ageing could be observed very clearly from the measured microstructural morphologies. The aged bitumen displayed a less rich microstructure with an almost bimodal size distribution of small (debris) and large elliptical domains (the stiffer phase). Moreover, a third, weaker phase appeared in the aged sample as small circular spots and arc-like features. The exact nature of this tertiary phase will be subject of further  
20 research. Nevertheless, it can be safely concluded that the influence of ageing on bitumen at the microstructural level can be studied by AFM. Future time dependent in situ ageing studies of binders with AFM are planned to gain deeper understanding on the ageing kinetics of bitumen. From the results presented one can also conclude that rheological changes in bitumen can be correlated with changes in the material's microstructure.

25 Upon addition of 20% BM1 bitumen the microstructure of the blend closely resembles the microstructure of the virgin bitumen, i.e. from a microstructural point of view the ageing process has been rolled back, which is in agreement with the findings from rheology. However, the earlier mentioned tertiary phase remains visible, and even a quaternary phase is observed. These new phases constitute only a small fraction of the microstructure, and their origin will be subject to future study.

30 Addition of the other rejuvenator, CM1, shows a completely different impact on the microstructural level. The stiffer elliptical domains are replenished, and needle-like particles form an interfacial phase between those domains and the matrix. The needle-like features are composed of nano-sized filaments, which also happen to occur sometimes independently. At higher doses the interfacial network phase is observed to become thicker, and the microstructure of aged bitumen rejuvenated with  
35 CM1 show ordering over time, at least in the first week after blending and most pronounced for lower additive dose rates.

Overall it is concluded that both rejuvenators show the rheological performance that is desired. Nevertheless, the mechanism leading to the softening and rejuvenation of the aged binder is very different, which can be inferred from the AFM observations. More experimental, modeling and  
40 interpretative work has to be done to unravel the mechanisms leading to the observations reported here. This also includes the investigation of the impact of various laboratory ageing scenarios compared with field aged materials. Finally, a deeper understanding of the underlying physico-chemical mechanisms contributing to the rejuvenation process will eventually lead to *optimized design strategies for effective and durable methods and materials* for service life enhancement as well as recyclability of pavement  
45 materials.

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