Benefits of F-T wax based warm asphalt mixes for short-term binder aging and pavement durability

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ABSTRACT

Wax based warm mix additives are increasingly applied to enable asphalt mixing and paving at lower temperatures or to improve the workability and compactability of hot-mix asphalt at conventional temperatures. The effects of these wax additives on the rheological behaviour and mechanical properties of bitumen and asphalt were already extensively investigated. Effects on the chemical properties of bitumen, such as aging, are largely unknown. For evaluating the effects of F-T wax, 50/70 bitumen was modified with F-T wax and analysed after short term aging (RTFOT). RTFOT at 163°C simulated the asphalt mixing and paving at conventional temperature. Warm mix conditions were simulated by RTFOT at 143°C in order to consider the lower mixing temperatures in the plant.

The aging of the binders was characterised by measuring rheological properties (DSR, penetration, softening point), chemical analysis (IR spectroscopy; SARA chromatography) and analysis of the colloidal components (asphaltenes fractionation).

The results show that the chemical composition is only determined by the bitumen characteristics. F-T wax modification significantly influences the mechanical properties after ageing. Compared to the unmodified binder, wax modification results in decreased effects of ageing on the shear properties in the complete service temperature range. The warm mix aging simulation indicated the significantly reduced aging and the resulting potential for increased pavement durability by applying wax additives.

Keywords: Additives, Ageing, Rheology, Warm Asphalt Mixture

1. INTRODUCTION

During mix production, hot storage, transport, paving and compaction processes, the bitumen used in the hot or warm mix asphalt is subjected to short term ageing. The effects of ageing can be observed by increased stiffness and viscosity of the binder and also the resulting asphalt mixture [1]. This stiffening effect of the bitumen is usually related to structural, volatile and oxidative effects. While structural effects are identified by rearrangements of the binder molecules, oxidation will affect the chemical composition of the bitumen whereas volatile substances of the binder are reduced at high temperatures.

The physical characteristics of a bituminous binder are directly associated with its chemical composition. However, the chemical nature of bitumen is a complex system of a multitude of different hydrocarbon molecules [1]. The chemical composition of bitumen can simplistically be characterised with a colloidal model. It allows the examination of the thermo-rheological properties of bitumen and is based on the theory that colloids with high polarity (asphaltenes) are peptized to micelles in an oily phase with lower polarity, called maltenes [2]. According to Zenke [3] the type of the asphaltenes (defined as asphaltenes with low, medium and high solubility) as well as their proportions significantly affect the overall mechanical properties of bitumen. Ageing usually results in a decrease of the maltene proportion while the composition of the three asphaltene types is shifted to the ones with lower solubility. The higher the temperature of the bitumen, the higher are the oxidative and volatile effects occurring during bitumen ageing.

Hot mix asphalt is usually produced at elevated temperatures as this is required for reaching adequate low binder viscosity which allows the mixing with aggregates and laying and compaction of the mix. In order to reduce energy requirements and in order to increase the reliability of road construction process under adverse weather conditions, warm-mix asphalt methods were developed. One successfully applied WMA technology is the modification of bitumen with low proportions (1-3 %) of waxes. This modification affects the binder viscosity in the wax crystallisation temperature range. Above this temperature, the wax is liquid and reduces the resulting binder viscosity significantly allowing the asphalt mix production at lower temperature. The specific properties of Fischer-Tropsch wax (F-T wax) allow for the reduction of production and paving temperatures of asphalt mixes of between 20 °C and 30 °C. Below the crystallisation temperature the wax crystals are dispersed in the bitumen matrix which results in an increase in viscosity. This stiffening effect is beneficial at elevated pavement service temperatures and results in increased resistance against rutting and even may allow early opening of the new road structure for traffic. However, increased binder stiffness is usually linked to increased cracking susceptibility of the pavement. In bitumen specification systems this is addressed by requirements regarding aged binder samples.

Bitumen according to EN 12591 has to reach requirements regarding resistance against short-term ageing as analysed in the laboratory by the rolling thin film oven test (RTFOT) according to EN 12607-1. In order to simulate the ageing occurring during the production of hot-mix asphalt, the ageing temperature is usually 163 °C. However, warm mix asphalt (WMA) allows the production of asphalt mixtures at reduced temperatures.

The modification of bitumen with F-T wax does not significantly change the ageing susceptibility of the bitumen [4]. One of the investigated F-T waxes even improved the long-term ageing properties. However, when considering the reduced WMA production temperature, the question is raised whether the application of WMA technology further reduces short-term ageing.

The effects of F-T wax in combination with different ageing procedures were simulated for hot and warm mix asphalt by modifying a 50/70 bitumen and subjecting it to short term ageing using the rolling thin film oven test (RTFOT). Besides the standard ageing temperature of 163 °C, effects of applying warm-mix ageing conditions in the RTFOT were evaluated at 143 °C (modified RTFOT ageing).

2. EXPERIMENTAL

2.1 Materials and ageing procedure

In order to evaluate the effects of the application of warm mix temperatures on the ageing characteristics of bitumen by using a F-T wax additive with congealing point 101°C, a 50/70 penetration grade bitumen was selected [6]. The bitumen sample was modified by the addition of 3 wt. % of F-T wax to the heated (160 °C) bitumen and homogenized by stirring for 10 minutes.

Two laboratory ageing procedures were carried out in order to simulate short-term ageing. Besides the standardised procedure for short term ageing by RTFOT (EN 12607-1) at 163°C, a modified RTFOT was applied with reduced temperature (143 °C) for simulating warm mix asphalt production conditions. The samples evaluated in this study are listed in Table 1.

Table 1: sample identification (binders with F-T wax)

Wax content	0% (neat)	3%
unaged	1.1	3.1
RTFOT (163 °C)	1.2	3.2
Mod. RTFOT (143 °C)	-	3.3

2.2 Conventional bitumen characteristics

The ring and ball softening points were measured according to the EN 1427 and the penetration according to EN 1426.

2.3 DSR temperature sweep

The rheological properties of fresh and aged binders were evaluated by Dynamic Shear Rheology, using plate-plate tests according to EN 14770.
The DSR tests were conducted in two temperature ranges at one frequency of 1.59 Hz and a deformation of 0.05 %. Cylindrical samples with a diameter of 25 mm and a height of 1 mm were tested for temperatures between 30 °C and 90 °C. Specimens with a diameter of 8 mm and a height of 2 mm were used for the test temperatures between -30 °C and +30 °C. In both cases, the temperature sweep was started at 30 °C.
Additionally, DSR samples of pure F-T wax were prepared and also tested in a temperature range of -10 °C to 90 °C.

2.4 Compositions of asphaltenes

The compositions of asphaltenes in terms of low, medium and high solubility are measured by a dissolution/ precipitation procedure [5] with three different solvent combinations of iso-octane and cyclohexane, see Table 2. The compounds not included in the three asphaltene fractions are the maltenes, soluble in iso-octane.
In this study the separation between maltene and asphaltene phases is defined by the solubility in iso-octane. The results of this study do not necessarily correspond with maltene/asphaltene separations based on other solvents.

Table 2: Fractions depending on order of solvents

Asphaltene solubility	Solvent	Solubility parameter δ_s $[MJ/m^3]^{1/2}$
High solubility	Iso-octane	14.0
Medium solubility	Iso-octane/cyclohexane (4:1)	14.8
Low solubility	Iso-octane/cyclohexane (1:1)	15.7

2.5 Infrared spectroscopy

FTIR spectra of the binders were determined by the transmission technique by measuring the IR-spectra of the dissolved bitumen samples as 5 wt. % solution in CCl_4 and in 0.5 mm layer thickness. Additionally the attenuated total reflection (ATR) procedure was applied directly on the pure, undissolved bitumen samples.
For the assessment of the ageing characteristics of the bitumen samples the peaks at a wave number of 1700 cm^{-1} were measured representing carbonyl (C=O) groups in the samples which are formed due to oxidative ageing of the bitumen.

2.6 Differential scanning calorimetry (DSC)

DSC was used to investigate the crystallization and melting behaviour of the F-T wax modifier in the binders. About 8-10 mg binder samples were placed in aluminium crucibles using empty crucibles as reference and nitrogen as inert gas atmosphere. After the first heating to 150°C for equalizing the thermal history, the samples were cooled and heated at 10 K/min. The detected peaks in the thermograms were integrated for determining the crystallization and melting enthalpies of the F-T wax additive in the bitumen. The bitumen itself does not exhibit phase changes in the investigated temperature range.

3. RESUTLS AND DISCUSSION

3.1 Conventional bitumen characteristics

The results of the conventional bitumen tests are given in Table 3. The addition of F-T wax to binder increases the softening point of the 50/70 bitumen by + 23.2°C. The oxidative ageing caused an increase of the softening point of the neat bitumen of 7.8 °C under RTFOT (163 °C).. Modified RTFOT (143 °C) conditions caused an increase of just 4.8 °C to the softening point with a resultant value of 78.8 °C.
The addition of F-T wax to the binder decreases the penetration by -17 [1/10mm]. The ageing caused a decrease of the penetration of the neat bitumen of -20 [1/10mm] due to RTFOT (163 °C). A higher penetration is recognized after modified RTFOT (143 °C) with a small decrease of -10 [1/10mm] compared to penetration after RTFOT (163 °C) for the modified binder.

The proportional change of the bitumen properties after ageing compared to the unaged values is added in table 3. For the softening point the standard RTFOT ageing procedure results for the wax modified binder in a smaller relative change compared to the neat bitumen. The same proportional decrease in penetration due to ageing can be observed for both binders.
The modified ageing at 143 °C results in significantly reduced changes of the conventional bitumen characteristics.

Table 3: Results of softening point ring and ball tests

Bitumen 50/70	$T_{R\&B}$ [°C]		Penetration [1/10 mm]	
Wax content	**0% (neat)**	**3%**	**0% (neat)**	**3%**
unaged	50.8	74.0	50	33
RTFOT (163°C)	57.6	81.8	30	20
Mod. RTFOT (143°C)	-	78.8	-	23
Change (163 °C)	13 %	11 %	-40 %	-39 %
Change (143 °C)		7 %		-30 %

3.3 DSR temperature sweep

In Table 4 the shear moduli (*G** in absolute number and as *log G**, given in brackets) and phase angles are given that were obtained at temperatures of -30 °C and 0 °C at DSR tests on specimens with a diameter of 8 mm and a height of 2 mm. The results obtained for 30 °C, 60 °C and 90 °C were measured on a sample with 25 mm diameter and 1 mm height. All tests were conducted at a frequency of 1.59 Hz. Note that two different types of rheometers were used for the two temperature ranges.

Table 4: Results of DSR Test: Complex shear modulus |G*| and phase angle δ obtained at the temperatures -30°C, 0°C, 30°C, 60°C and 90°C and a frequency of 1.59 Hz

<table>
<tr><th rowspan="2">Specimen (D/h) [mm]</th><th rowspan="2">T [°C]</th><th rowspan="2">Ageing stage</th><th colspan="3">Shear modulus |G*| (1.59 Hz) [Pa]
(in brackets: log G*)</th><th colspan="3">Phase angle δ [°]</th></tr>
<tr><th>0%</th><th>3%</th><th>Pure F-T wax</th><th>0%</th><th>3%</th><th>Pure F-T wax</th></tr>
<tr><td rowspan="6">8/2</td><td rowspan="3">-30</td><td>Unaged</td><td>353,574,198 (8.6)</td><td>260,527,484 (8.4)</td><td>-[1)]</td><td>7.1</td><td>13.3</td><td>-[1)]</td></tr>
<tr><td>RTFOT (163°C)</td><td>351,102,504 (8.6)</td><td>259,315,639 (8.4)</td><td rowspan="2">-[2)]</td><td>7.4</td><td>11.2</td><td rowspan="2">-[2)]</td></tr>
<tr><td>RTFOT (143°C)</td><td>-[2)]</td><td>356,729,707 (8.6)</td><td>-[2)]</td><td>7.0</td></tr>
<tr><td rowspan="3">0</td><td>Unaged</td><td>65,904,545 (7.8)</td><td>81,339,821 (7.9)</td><td>49,372 (4.7)</td><td>29.2</td><td>23.4</td><td>12.3</td></tr>
<tr><td>RTFOT (163°C)</td><td>76,705,686 (7.9)</td><td>84,655,375 (7.9)</td><td rowspan="2">-[2)]</td><td>26.5</td><td>21.9</td><td rowspan="2">-[2)]</td></tr>
<tr><td>RTFOT (143°C)</td><td>-[2)]</td><td>90,026,844 (8.0)</td><td>-[2)]</td><td>22.6</td></tr>
<tr><td rowspan="9">25/1</td><td rowspan="3">30</td><td>Unaged</td><td>514,753 (5.7)</td><td>2,706,434 (6.4)</td><td>80,772 (4.9)</td><td>68.1</td><td>48.2</td><td>14.0</td></tr>
<tr><td>RTFOT (163°C)</td><td>1,045,897 (6.0)</td><td>3,902,878 (6.6)</td><td rowspan="2">-[2)]</td><td>60.2</td><td>43.6</td><td rowspan="2">-[2)]</td></tr>
<tr><td>RTFOT (143°C)</td><td>-[2)]</td><td>2,056,177 (6.3)</td><td>-[2)]</td><td>53.1</td></tr>
<tr><td rowspan="3">60</td><td>Unaged</td><td>3,250 (3.5)</td><td>56,639 (4.8)</td><td>256,654 (5.4)</td><td>85.2</td><td>48.3</td><td>26.9</td></tr>
<tr><td>RTFOT (163°C)</td><td>8,039 (3.9)</td><td>67,247 (4.8)</td><td rowspan="2">-[2)]</td><td>80.9</td><td>57.4</td><td rowspan="2">-[2)]</td></tr>
<tr><td>RTFOT (143°C)</td><td>-[2)]</td><td>21,032 (4.3)</td><td>-[2)]</td><td>68.3</td></tr>
<tr><td rowspan="3">90</td><td>Unaged</td><td>109 (2.0)</td><td>2.289 (3,4)</td><td>1,190,996 (6.1)</td><td>90.0</td><td>47.5</td><td>24.0</td></tr>
<tr><td>RTFOT (163°C)</td><td>210 (2.3)</td><td>664 (2.8)</td><td rowspan="2">-[2)]</td><td>89.5</td><td>72.2</td><td rowspan="2">-[2)]</td></tr>
<tr><td>RTFOT (143°C)</td><td>-[2)]</td><td>616 (2.8)</td><td>-[2)]</td><td>70.9</td></tr>
<tr><td colspan="9">[1)] F-T wax specimen could be tested down to -10 °C during cooling
[2)] Ageing procedure was not applied for the sample</td></tr>
</table>

The complex shear moduli are plotted versus the temperature in Figure 1. Phase angles are shown in Figure 2.
The addition of F-T wax increases the shear modulus of the bitumen in the unaged stage considerably. When comparing the shear modulus of the unaged neat bitumen (1.1) with the unaged modified binder (3.1) in Figure 1, it can be observed that the stiffening effect caused by wax modification increases with temperature. Below 0 °C the effect of wax modification is very small as identified by log G* values added in the table. The shear modulus results obtained on the pure F-T wax sample were measured only for the temperature range between -10 °C and 90 °C and show higher shear moduli compared to the unmodified bitumen at temperatures above 30 °C. This explains the increasing stiffening effect of wax modification at elevated temperatures. At lower temperatures the bitumen shear modulus is higher than the stiffness of the wax. Still, a significant shear modulus increase can be observed. This effect is postulated to be related to additional structural effects of the wax modification because the pure wax stiffness is lower compared to the shear modulus of the pure bitumen at temperatures below 30 °C.

The shear moduli and phase angles measured on pure wax samples are added to the diagrams. Compared to bitumen, the wax stiffness is less temperature dependent. With decreasing temperature, the phase angle as well as the shear modulus decreases. However at low temperatures the phase angle (T< 10 °C) as well as the shear modulus (T< 0 °C) increase.
Regarding the effect of ageing, the shear modulus of the unmodified bitumen is increased by RTFOT (sample 1.2 vs. 1.1). Considering the logarithmic scale in the G* plot (Figure 1) it can be observed that the stiffening effect of ageing is small at a temperature below 0 °C and becomes larger with increasing temperature. Below 0 °C the ageing effect is negligible.

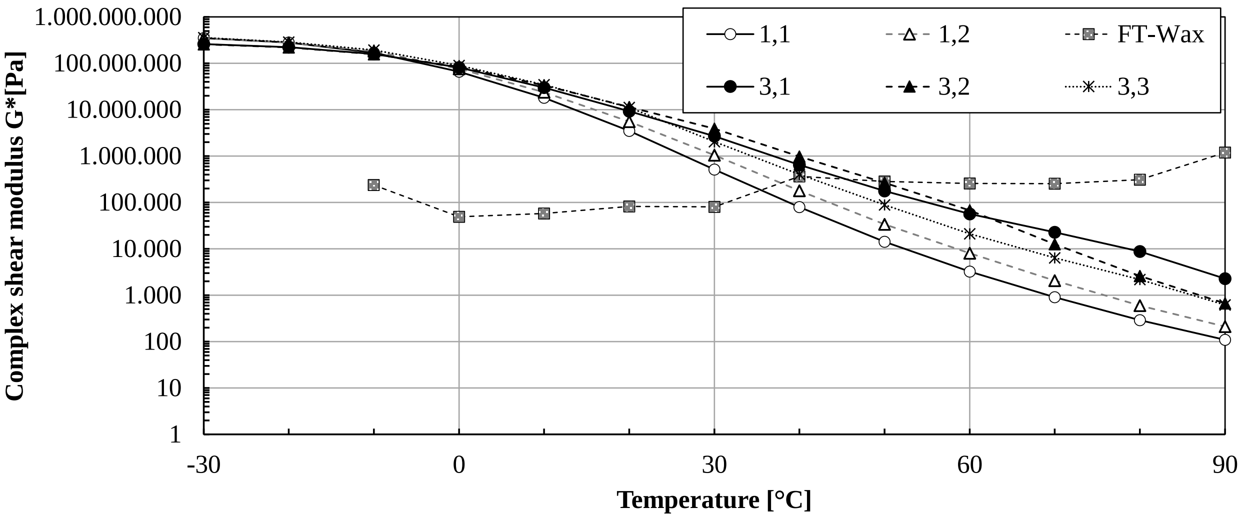

Figure 1: Complex modulus versus temperature measured at 1.59 Hz

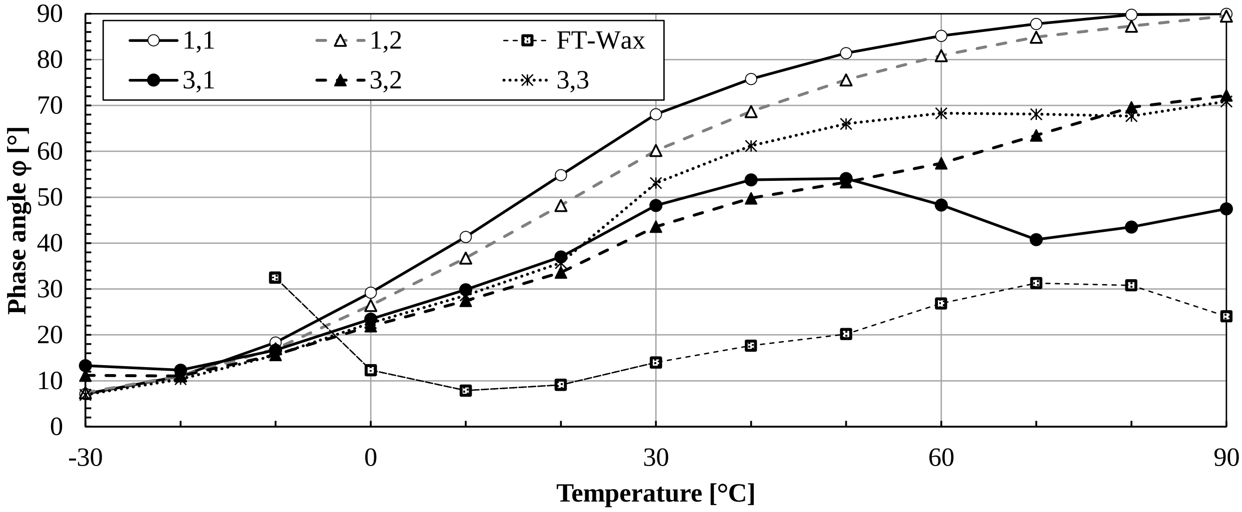

Figure 2: Phase angle versus temperature measured at 1.59 Hz

The wax modification changes the effects of ageing significantly. Standard RTFOT ageing at 163 °C results in comparably small changes of G* (sample 3.2 vs. 3.1). At test temperatures below 60 °C the shear modulus is increased. However, at temperatures above 60 °C significantly lower shear modulus values are obtained after RTFOT ageing.
The modified RTFOT ageing at 143 °C results in an increase of the shear modulus only at temperatures below 30 °C (sample 3.3 vs. 3.1). Above this temperature again a significant decrease of G* compared to the unaged samples is obtained.
The addition of F-T wax to bitumen results in a decrease of the phase angle for test temperatures above -20 °C which can be interpreted as a shift towards more elastic and less viscous material performance. Due to the decreasing bitumen viscosity with increasing temperature also the phase angle of the wax modified bitumen is increasing but reaches a local maximum value at approx. 50 °C. Between 50 °C and 70 °C the phase angle is decreasing which can be explained by increasing differences between the moduli of the bitumen and the wax network, which therefore predominates the overall viscoelastic properties. At a temperature of 70 °C the wax begins to melt which again results in an increase of the phase angle. This temperature-dependent phase angle results in a typical ‘bulge’.

After ageing, the phase angle measured on the unmodified binders is decreased representing reduced viscous material properties (sample 1.2 vs. 1.1). For the F-T wax-modified binder again the temperature-dependent phase angles indicate structural effects. Ageing at 163°C (sample 3.2 vs. 3.1) also shows a phase angle decrease for temperatures below of 50 °C. Above this temperature the structural effects of the wax results in higher phase angle values after ageing. However the specific 'bulge' indicating the structural effects of melting wax compounds as observed in the unaged sample 3.1 is not observed.
After modified RTFOT ageing with reduced temperature of 143 °C, the wax modified bitumen still shows the specific phase angle "bulge" (sample 3.3) – however it is less pronounced compared to the unaged sample (3.1). For the reduced ageing temperature the ageing results in increased phase angle above a temperature of 20 °C.
The wax-modified binder shows some abnormalities after ageing. In order to check if these results can be explained by structural effects due to wax crystallization, additional chemical tests were conducted.

3.4 Asphaltene composition

The results of the precipitation experiments to differentiate three asphaltenes, total asphaltene and maltene contents of all unaged and aged binders are presented in figure 3.
When comparing the unaged samples 1.1 and 3.1 it can be observed that the wax modification does not significantly change the proportions of maltenes and asphaltenes of varied solubility. The proportion of low soluble asphaltenes in the wax-modified sample is slightly increased compared to the non-modified binder.
The short-term ageing by RTFOT decreases the total maltene contents and increases the total asphaltene contents.
With regard to the proportions of the three types of asphaltenes, the neat (1.1) as well as the wax modified binder (3.1) show in the unaged stage a maximum of medium soluble asphaltenes. An increase of low soluble asphaltenes can be recognized during RTFOT ageing at both temperatures for both binders.
The modified RTFOT (143 °C) results in a colloidal composition in between of the unaged (3.1) and RTFOT aged binder (3.2).

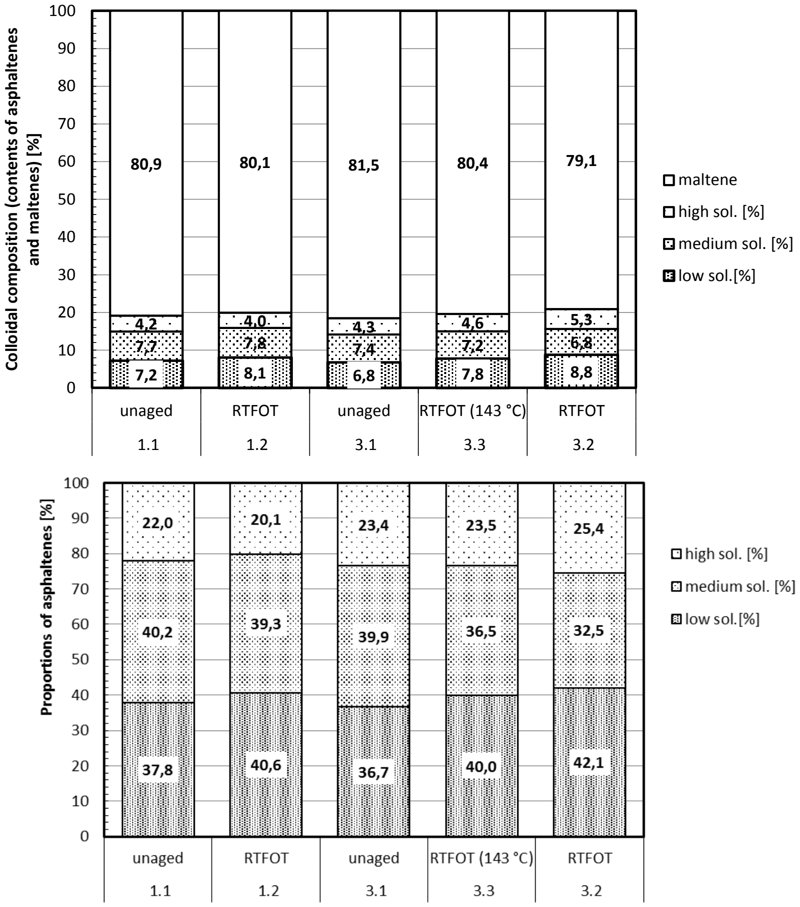

Figure 3: Content of low, medium, high soluble asphaltenes and maltenes in the binder samples (left) and proportions in the asphaltene fraction (right)

3.5 Results of Infrared (IR) Spectroscopy

IR spectroscopy investigations by transmission and ATR techniques (Figure 4) were carried out to observe the oxidation progress. The IR spectra of the unaged and aged binders differed mainly in the wave number range around 1700 cm^{-1} which represents carbonyl groups (C=O) that result from oxidation. Figure 4 shows details of the IR spectra obtained from the transmission and ATR experiments for the C=O peak range. After RTFOT at 163 °C, the absorption in the C=O-range was slightly intensified. RTFOT at a temperature of 143 °C caused even smaller absorptions.

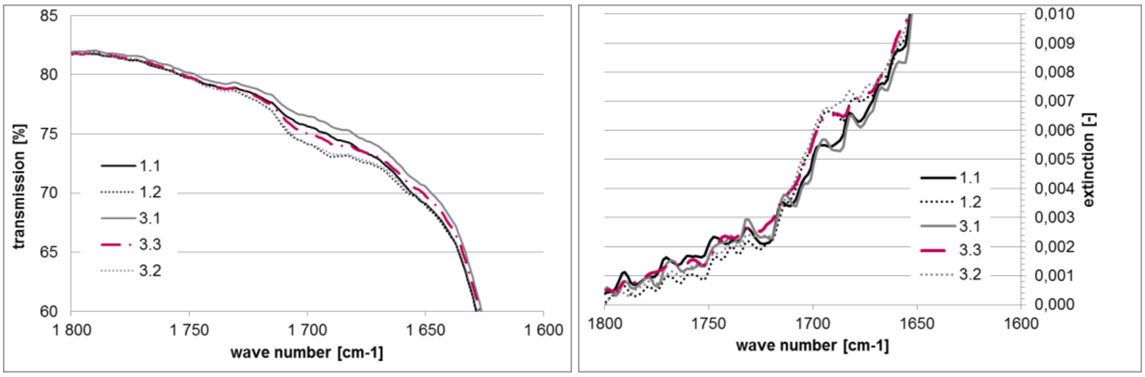

Figure 4: FTIR spectra (detail in 1700cm^{-1} range) of unaged and aged binders using transmission (left) and ATR (right) techniques

In order to quantify the extent of oxidation, the areas of the C=O peaks were integrated. In Figure 5 the C=O peak areas as evaluated from the transmission and ATR experiments for the five binder samples are shown. The unmodified and the F-T wax modified binders were oxidized with comparable intensity and the visual impression of stronger oxidation at 163°C (sample 3.2) in comparison to 143°C (sample 3.3) was confirmed.

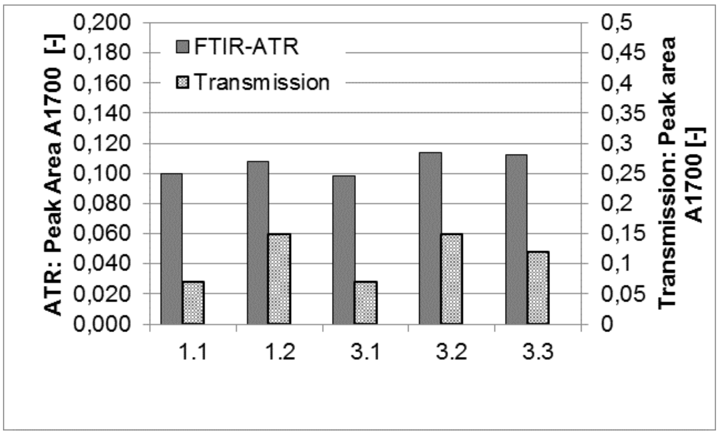

Figure 5: Peak areas of FTIR spectra in the carbonyl range (1715 – 1682 cm-1) at different ageing stages

3.5 Results of differential scanning calorimetry

In Figure 6 the results of DSC tests are plotted. When the test is run in the heating mode (upper curves) it can be observed, that the major part of the wax melts between 90 °C and 105 °C. In the cooling mode (lower curves), the main part of the crystallisation occurs between 85°C and 70°C.

Here the unaged sample 3.1 displays the most distinct peak resulting in a crystallisation enthalpy of 3.89 J/g. After RTFOT ageing these values are reduced to 3.46 J/g (at 143°C) and 3.23 J/g at 163°C indicating decreasing crystallinity of the wax by aging.

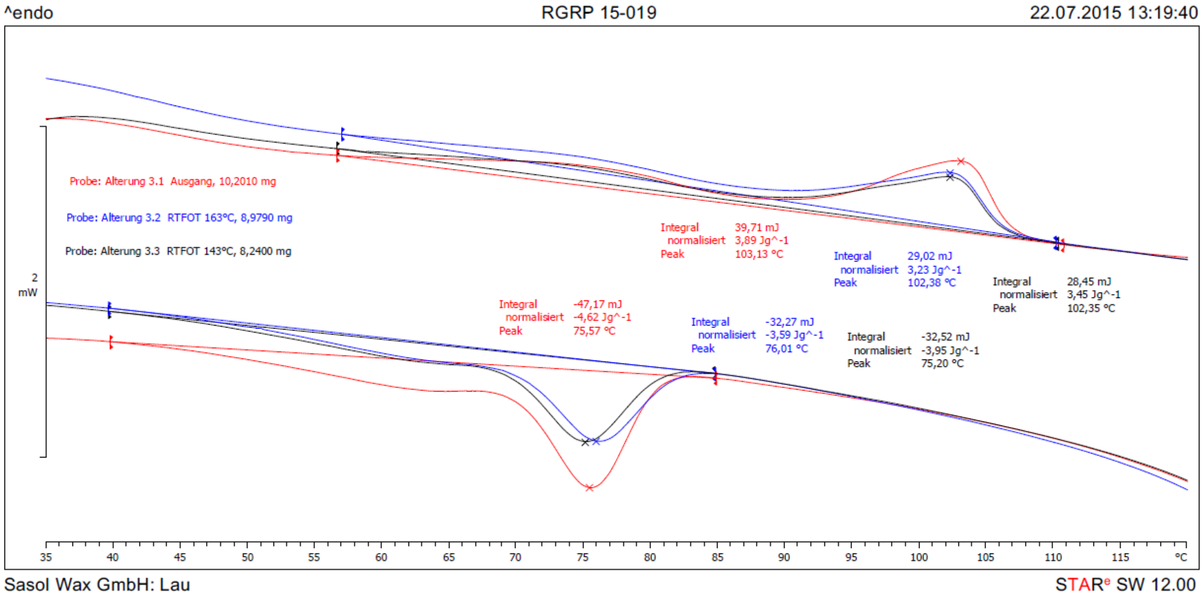

Figure 6: DSC thermograms of unaged (3.1), RTFOT 163°C (3.2) and RTFOT 143°C (3.3) aged F-T wax modified binder. Heating rate 10 K/min

4. Discussion

4.1 Effects of ageing on neat bitumen

Ageing usually increases the stiffness of the bitumen (for example its shear modulus) due to a decreasing content of volatile bitumen compounds and the formation of larger molecules due to oxidation. This results in decreased penetration and increased softening point as can clearly be observed for the neat bitumen sample (refer to Table 3).
For evaluating the stiffening effect by modification and/or ageing, the proportional change in shear modulus can be calculated. For further coping with the exponential effects on shear properties, a stiffening index is defined by equation (1):

$$SI = \frac{\log G^*_{mod} - \log G^*_{ctr}}{\log G^*_{ctr}} \cdot 100\ [\%] \qquad (1)$$

where
SI: Stiffening index,
G^*_{mod}: Shear modulus of modified or aged sample,
G^*_{ctr}: Shear modulus of control sample (e. g. unmodified / unaged).

As plotted in Figure 7, the ageing stiffening effect in the neat bitumen is considerable stronger at elevated service temperatures compared to low temperatures. The applied short-term ageing affects the rheological properties of bitumen more at high temperatures. This can be explained by the overall temperature-dependency of the bitumen rheology. Whereas small temperature changes result in high variability of the stiffness modulus in the elevated service temperature range, the shear modulus has an asymptote at very low temperature ("glass modulus"). At low service temperature conditions the overall variability of the shear modulus is smaller and therefore also ageing effects are lower.

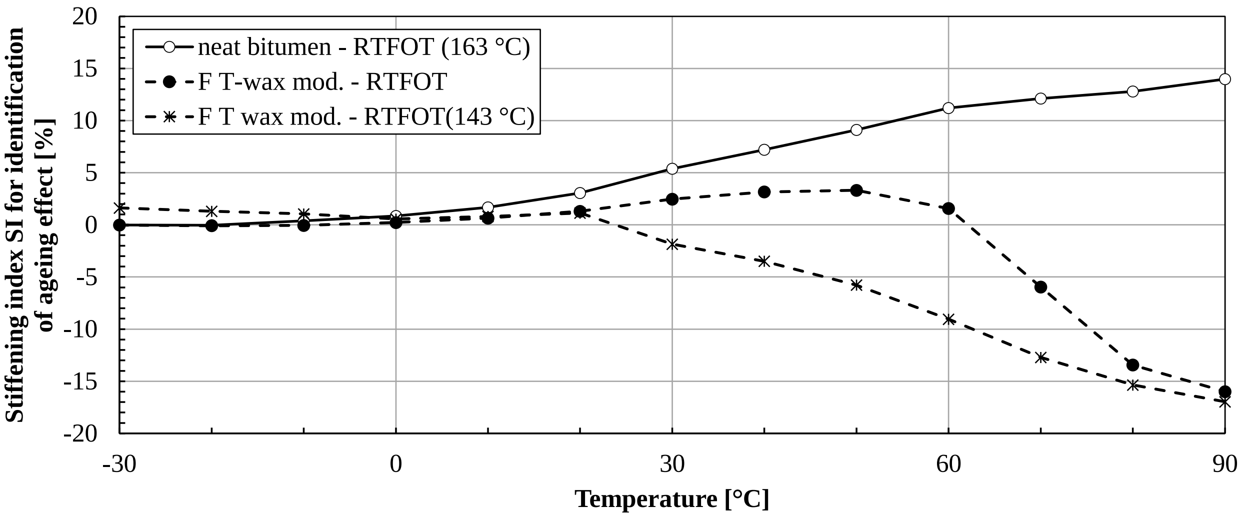

Figure 7: Proportional effect of ageing on (log G*) for neat and F-T wax-modified bitumen as identified by stiffening index SI.

4.2 Effects of wax modification

The results of the conventional bitumen characterisation (ring and ball softening point and penetration) clearly indicate the stiffening effect of the bitumen modification with F-T wax. This effect can also be observed by an increase of the shear modulus as well as in a shift from viscous to elastic properties identified by a decrease of the phase angle. However, as the DSR tests conducted at a wide range of temperatures show, this stiffening effect is significantly stronger at higher service temperatures, whereas at low temperatures, the initial bitumen viscosity predominates the stiffness of the modified binder.
The results of the chemical test methods indicate that the wax modification does not affect the colloidal proportions of maltenes and various asphaltene fractions. This is also shown in Figure 8, indicating the asphaltene composition of the evaluated samples in comparison to other samples of 50/70 penetration grade bitumen types of various sources. The effect of wax modification (sample 3.1 vs. 1.1) is far lower compared to the diversity of bitumen samples of the same specification (50/70) from various sources and crudes. Therefore, the significant effect of wax modification on the mechanical properties of bitumen is not caused by a change of the colloidal system but has other structural reasons.

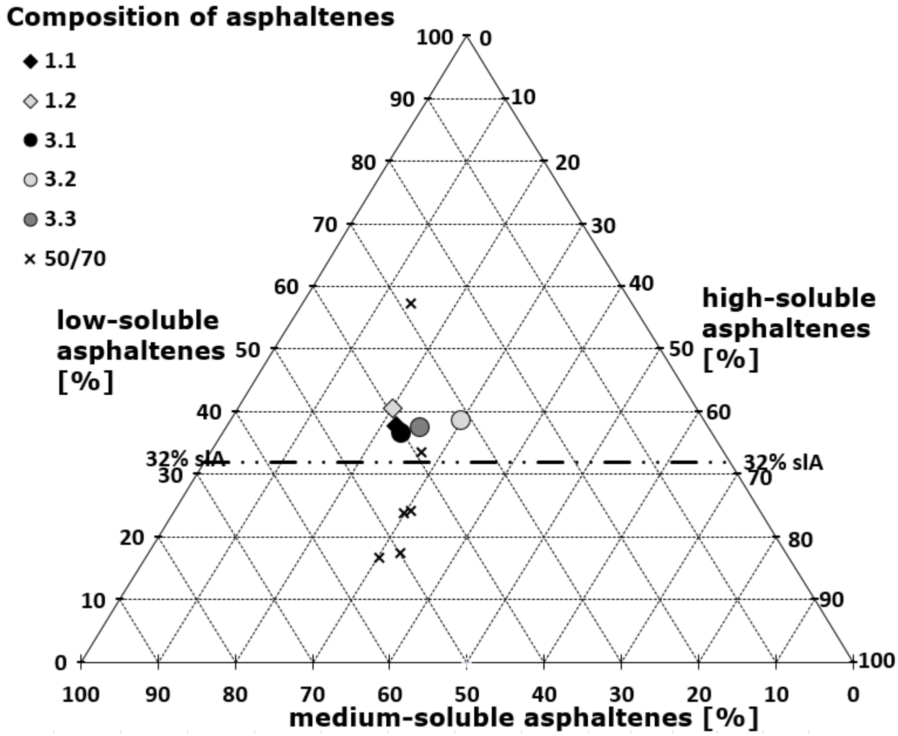

Figure 8: Asphaltene composition of the analysed samples compared to various unaged 50/70 samples

As identified for the conventional tests, the modifier will affect the binder properties significantly stronger compared to the effect of ageing. However, as identified in Figure 9, the effect of F-T wax modification is strongly influenced by temperature. Here the stiffening index represents the difference between neat and modified bitumen. In unaged samples the modification will result in a stiffening index (SI) up to 65 % (note, in non-logarithmic scale this equals to a shear modulus increase of 3000 %). However, the stiffening effect is highly influenced by temperature. At temperature below -10 °C the shear modulus of F-T modified samples is even smaller compared to the neat bitumen. This can be explained by the shear stiffness of F-T wax after crystallization, which is compared to bitumen less dependent on temperature. Especially at temperatures below 30 °C (unaged binder) or 60 °C (aged binder), the wax shear modulus is smaller compared to the neat bitumen shear modulus which results in decreased stiffening or even in a stiffness decrease as observed at temperatures < -10 °C for the RTFOT-aged F-T wax modified bitumen (compare Figure 1).
Especially at moderate and high service temperatures the test results of the conventional methods (softening point, penetration) are primarily controlled by the wax modifier and, therefore, cannot be applied for identifying the ageing state of the bitumen compounds.

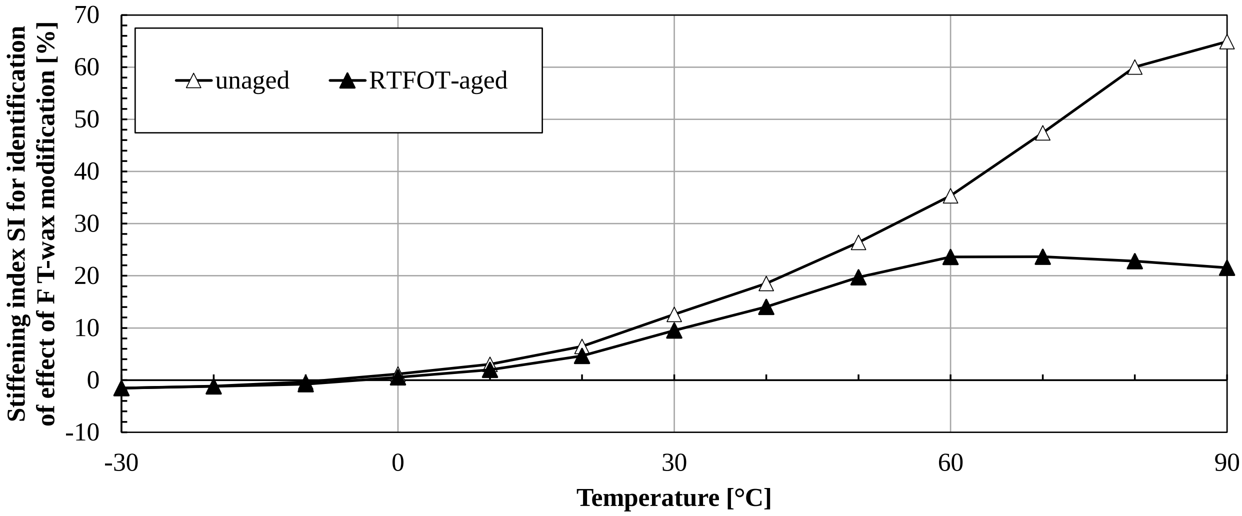

Figure 9: Stiffening index SI for identifying the effect of F-T wax modification on G* in logarithmic scale in unaged and RTFOT-aged condition.

4.3 Effects of ageing on F-T wax modified bitumen

For identifying the shear stiffness effect of ageing on neat and F-T wax modified binders, the stiffening index is plotted in Figure 7, see section 4.1. Unaged binder samples were used as control samples. Ageing increases the shear modulus of neat bitumen over the whole temperature range. The resulting stiffening index increases with temperature from 0 % to 14 %. However, for the F-T wax modified samples the ageing results in a negative stiffening index for higher service temperatures (> 60 °C for standard RTFOT, > 20 °C for modified RTFOT). Obviously ageing also affects the mechanical properties of the modifiers in the binder. At the same time, the modifiers will influence the chemical stability of the bitumen compounds. These effects can be observed in the results of mechanical and chemical measurements.

5. INTERPRETATION

5.1 Effects of F-T wax modification in temperature-domain

The evaluation of the mechanical properties within a large temperature range, as applied in DSR tests, usually allows a better identification of ageing effects. With increasing temperature, the wax-modified bitumen (sample 3.1) indicates increased phase angle values up to a temperature of 50 °C. With further temperature increase up to 70 °C, a decrease of the phase angle can be observed. With higher temperature, again a phase angle increase was measured. This observation is a clear sign for the specific structural effects of the wax modification. Above 70 °C already the effect of wax melting will result in more viscous properties and therefore is responsible for increased phase angles, as also indicated by the DSC test results. Below 50 °C the bitumen's shear stiffness is higher than the stiffness of the wax network and, therefore, the bitumen predominates the viscoelastic properties of the modified binder. Thus, the usually observed increase of phase angle with increase of temperature is also experienced in this study. Between 50 °C and 70 °C the decreasing phase angles indicate the structural interaction of bitumen and wax. With increasing temperature and, thus, decreasing bitumen viscosity, the wax structure, which is still crystallised, gains a stronger part of the overall mechanical properties of the modified bitumen.

5.2 Effects of RTFOT-ageing on F-T wax modified bitumen rheology

At test temperatures < 60 °C, the wax modified binder samples indicated the expected increase of the shear modulus and decrease of the phase angle after short-term ageing. From the asphaltene composition experiments, it can be observed, that the general bitumen colloidal properties are similar for both RTFOT-aged binders, the neat as well as the F-T wax modified. Below 60 °C, the pure F-T wax shear modulus is lower compared to the shear modulus of the aged bitumen and therefore the latter predominates the viscoelastic rheology of the modified binder.
However, at higher temperatures the shear modulus of the wax modified samples even indicates a decrease after ageing. Again, at these high temperatures the shear modulus represents the resulting stiffness of the wax network in the sample, whereas the increasing viscosity of the bituminous compounds still results in lower stiffness compared to the wax modification and therefore the ageing effect after RTFOT (163 °C) of the bitumen is not visible. However, the ageing results in lower wax stiffness and reduced elasticity and therefore in lower shear modulus but higher phase angle compared to the unaged wax-modified sample. This is an indication of an ageing effect on the wax crystal network itself resulting in reduced stiffening effect (compare also figure 9). A reason for this reduced stiffness can be found in reduced wax crystallinity and crystal size as shown by a reduced crystallisation enthalpy measured in DSC experiments. For an additional check, some microscopy trials were conducted. Therefore, pictures of the surface of prepared bitumen samples, which were cooled down in room conditions, were taken with a stereoscope (see figure 10). The neat binder shows a very homogenous, dark surface (the white dots are dust particles) which is not visibly influenced by ageing (top row). However, the samples modified with F-T wax clearly show a bright structure on the sample surface (bottom row). These structural elements are comparably large in the unaged sample (left) but become finer with proceeding ageing. It can be observed, that the RTFOT-aged sample (right) indicates a finer structure compared to the sample after modified RTFOT-ageing after 143 °C.

5.3 Effects of modified RTFOT (143 °C) on F-T wax modified bitumen

As identified by the negative stiffening index in Figure 7, the shear modulus after modified RTFOT (143 °C) of the F-T wax modified binder decreases at temperatures above 20 °C compared to the unaged sample. Simultaneously, higher phase angles are observed compared to the unaged F-T wax modified sample. Again the interaction between aged neat bitumen (with a presumably resulting shear stiffness between the unaged and the RTFOT-aged values) and the F-T wax crystal network can be used for explaining this observation. At a temperature between 20 °C and 40 °C, the wax crystal network will result in higher shear modulus compared to the modulus of aged neat bitumen (not measured for an ageing temperature of 143 °C) and therefore predominates the overall rheology with increase of the shear modulus and decrease of the phase angle. Only at lower temperatures, the bitumen characteristics predominate. Also with modified ageing temperature, a reduced crystallization can be observed in DSC and microscopic experiments.

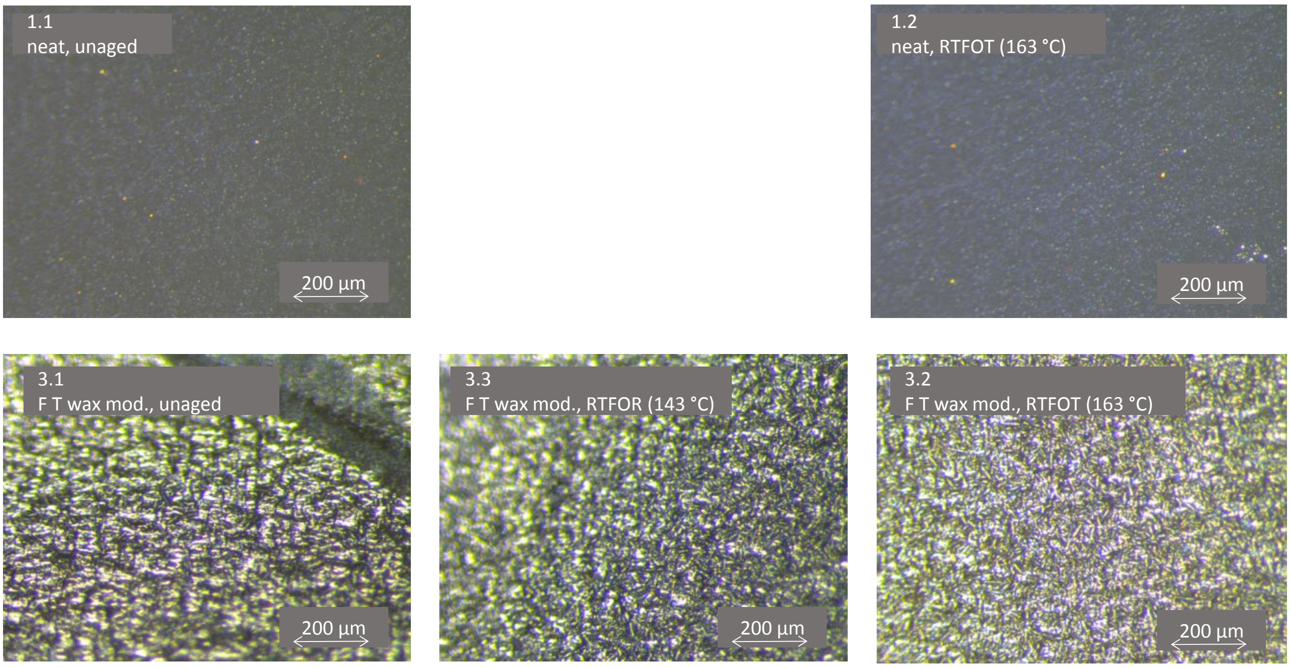

Figure 10: Results of stereoscopy for unmodified and modified binder samples before and after ageing

5.4 Ageing effect on F-T wax structure

The wax crystal structure is clearly affected by the ageing conditioning of the binders. The wax crystallization takes place during cooling of the wax-modified bitumen. As indicated by the DSC test results, the process starts at a temperature of 85 °C and proceeds until 70 °C. However, the sizes of the emerging crystals depend on the cooling rate and the viscosity of the material around the crystals. At high cooling rates, less time is available and only small crystals can be formed in the bitumen. During growth, the crystals need to displace bitumen compounds. The higher the viscosity of the bitumen, the slower is the growing process and thus the smaller are the wax crystals in the bitumen matrix. During the construction process of asphalt pavements, cooling rates of approx. -2 °C/min can be observed. Laboratory prepared bitumen samples are usually cooled in room conditions which results in similar cooling rates. On the other hand, usually the binder sample in DSR tests is cooled down after trimming by forced temperature-control very fast by a rate < -20 °C/min. Therefore, less time is available for forming crystals in wax modified samples.
The bitumen viscosity as a result from ageing conditioning also affects the crystal size. The RTFOT-aged bitumen has the highest viscosity and therefore it introduces the highest resistance against displacement by wax crystals. This results in smaller crystal size as observed in figure 10.

6. CONCLUSIONS

The following conclusions can be drawn from the results of the presented investigation:

- F-T wax modification does not significantly change the chemical composition and oxidation susceptibility of bitumen.
- The differences in the compositions of asphaltenes of binders from different sources are higher than effects from F-T wax modification and even RTFOT ageing.
- The stiffening effect of wax is larger at elevated service temperature but significantly lower at low service temperatures. Therefore, conventional bitumen characteristics obtained at elevated temperature (e. g. ring and ball softening point) are no indication for stiffening effects at other temperatures.
- Reduced short-term ageing temperature by WMA technology will reduce the ageing effect compared to standard short-term ageing conditions as clearly identified by the colloidal binder structure and the conventional bitumen properties.
- Modified RTFOT ageing at reduced temperature results in more viscous binder properties and in reduced phase angles over all test temperatures.
- The feasibility of ageing assessment on wax-modified bitumen using DSR has to be checked for kinetic effects due to possible influences of the cooling rate controlled wax crystallization during specimen preparation.

Especially the last conclusion should be investigated in more detail. Additional DSR tests with varied cooling rates after specimen trimming will be applied in future. These tests will be complemented by the microscopic assessment of freshly-broken sample surfaces in order to evaluate the wax crystal network size.

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