Effect of wax crystallization on complex modulus of modified bitumen after varied temperature conditioning rates

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Abstract. Most of European roads are paved with asphalt materials. Mechanical properties as well as durability depend on bituminous binder properties. To influence viscous binder properties wax additives are applied in asphalt mixture for reducing temperature during production process. The crystallization of wax additives results in a rapid viscosity changes within a small temperature span. This allows the reduction of asphalt mix temperatures as well as affects the complex modulus within the performance temperature range. In order to evaluate the effect of wax crystallization in bituminous binders, three binders of different viscosity are modified with 0%, 1.5% and 3% Fisher-Tropsch wax. For the rheological characterization complex shear modulus and phase angle are measured by variation of the cooling rate after sample trimming. Furthermore physical properties were determined by softening point ring and ball again with varied cooling of the bitumen sample after specimen preparation.

1. Introduction

The majority of European road network is paved with asphalt materials. Mechanical properties as well as durability depend on bituminous binder properties. To influence viscous binder properties wax additives are used in asphalt mixture for reducing temperature during production process. Wax additives show crystallization effects resulting in a rapid viscosity change within a specific temperature range. Above the crystallization temperature, binder viscosity is reduced significantly allowing lower mixing and compaction temperatures. Below the wax crystallization temperature, the viscosity of the modified binder is increased which results in improved rutting resistance.

The wax crystallization takes place during cooling in a temperature range between 80 °C and 100 °C for Fischer-Tropsch (FT) wax [1,5]. Within this temperature range, the time available for crystallization affects the size and type of crystallization. FT-wax consists of long hydrocarbon chains up to C₁₀₀ forming a lattice microcrystalline structure and crystallize as small needles in a small melting area [2]. The process of needle crystallization process of paraffin wax was studied by Rhodes et al. 1927 in detail [6]. Several fractions of paraffin wax from crude petroleum were analyzed by microscopy with a detailed view to crystallization process within fast and slow cooling rates. In dependence of the cooling speed the wax is solidifying in plates, generally. Rhodes et al. observed during rapid cooling rate that needles are developed by curling of the edges of the plates. The developing from wax crystal plates to needles can be seen in Figure 1.
In contrast to hypothesis in [1], Rhodes et al. described that during slow cooling over a period of several hours paraffin fractions solidify in plates with less potential to form well defined needles (Figure 2). The process of needle crystallization is very slow resulting in a loose structure with less defined needles.

Figure 2. Converting plate crystals to needles during crystallization process with slow cooling. [6]

In a previous publication [1] the effect of FT-wax modified binders by using different ageing procedures was investigated. On the one hand standard RTFOT ageing procedure was carried out to simulate ageing process of hot mix asphalt, on the other hand modified RTFOT ageing procedure at 143 °C was carried out to simulate warm mix ageing conditions. The complex modulus results showed an influence in the ageing stage (indicated as binder viscosity) on the viscosity changing effect provoked by wax modification. In aged binders less effects of the waxes were identified. The neat binder viscosity was estimated as responsible factor for these test result: Within (aged) binder of high viscosity, the wax crystallization is hindered by high bitumen viscosity which results in smaller wax crystals and therefore lower effects of the modification on the complex modulus.

2. Experimental

In order to validate this theory, a new experiment was designed, which results are discussed in this distribution. In order to validate the results discussed in [1], varied binders were tested in complex modulus with and without wax modification. In addition, the cooling rate between specimen trimming and complex modulus test temperature was varied. According to the drafted model [1], a fast cooling rate would result in a weak wax crystal network whereas slow cooling rates creates a strong crystal wax network. In order to evaluate the effect of wax crystallization in dependency of the binder viscosity, three penetration grade binders (20/30, 30/45 and 50/70) were modified by 0%, 1.5% and 3% FT-wax.

The complex modulus was assessed in DSR tests according to EN 14770 in temperature-sweep tests between 20 °C and 120 °C. After trimming of the specimens (diameter 25 mm, gap 1 mm) at a temperature of 80 °C above the softening point the temperature was increased to 120 °C. Then two different temperature conditioning procedures (TCP) were applied:

- TCP I included a slow cooling rate of 10 K/h from 120°C to 20°C simulating cooling conditions of asphalt layers in field.
TCP II included a fast cooling rate of 1.800 K/h from 120°C to 20°C as usually applied within DSR tests.

The temperature sweep tests were started at 20 °C and complex modulus was measured for 20, 30, 40… up to 120 °C with a frequency applied of 1.59 Hz.

The DSR tests were complemented by softening point ring and ball according to EN 1427. Again, in addition to standard procedure with non-controlled cooling a second set of samples were prepared which were cooled by applying a constant temperature rate of -10 °K/h within a temperature control chamber.

3. Results of DSR temperature sweep tests

The complex shear moduli G* and the phase angles δ versus the test temperature are plotted for assessed temperatures above 30 °C in Figure 3 to Figure 8. The results obtained at 20 °C showed some scattering and were not plotted for improving the readability of the figures. G* and δ measured on pure FT-wax samples after slow and fast cooling are included in the figures.

In Table 1 and Table 2 the shear moduli G* and phase angles δ are given for the test temperatures 20°C to 120°C with a temperature difference of 20 °C.

For the unmodified binders, the difference between complex modulus measured after slow and fast cooling are within ± 6 % and therefore neglectable. With increasing wax content, the effect of cooling rate is increasing. For the binders with 1.5 % added wax, the complex modulus measured after fast cooling rate (TCP II) is up to 80 % higher compared to the values measured at slow cooling rate (TCP I). With 3 % wax addition, this difference increases up to 250 %. The difference between fast and slow cooling rate is further affected by the viscosity of the neat bitumen. With decreasing viscosity (20/30 - 30/45 – 50/70), the differences between slow and fast cooling rate grow stronger.

The addition of wax results in a decrease of phase angle for temperatures below 110 °C indicating the stiffening effect of the crystalized wax within the bitumen. Regarding the effect of cooling rate, δ of the neat binders are only little higher after fast cooling compared to slow cooling. At test temperatures below 60 °C the binder samples with 1.5 % wax addition indicate higher phase angles (and therefore more viscous properties) when cooled down faster compared to slow cooling. At higher temperature, the fast cooling results in lower values of δ. The binders with 3 % wax modification indicate systematically lower phase angles for TCP II (fast cooling) compared to TCP I (slow cooling). As also observed for the complex modulus, this difference is highest for the bitumen 50/70.
### Table 1. Results for complex shear moduli G* [Pa].

| T [°C] | 0% wax | 1.5% wax | 3.0% wax | 0% wax | 1.5% wax | 3.0% wax | 0% wax | 1.5% wax | 3.0% wax |
|-------|--------|----------|----------|--------|----------|----------|--------|----------|----------|
| TCP I (slow) | TCP II (fast) | G*fast/G*slow [-] |
| 20 | 1497829 | 5256462 | 5230966 | 851142 | 3963015 | 3468841 | 0.57 | 0.75 | 0.66 |
| 40 | 631283 | 737190 | 854239 | 591865 | 847774 | 1153666 | 0.94 | 1.15 | 1.35 |
| 60 | 33859 | 45098 | 59128 | 32631 | 56307 | 98081 | 0.96 | 1.25 | 1.66 |
| 80 | 2544 | 3331 | 4409 | 2533 | 4764 | 9969 | 1.00 | 1.43 | 2.26 |
| 100 | 298 | 364 | 399 | 303 | 417 | 722 | 1.02 | 1.15 | 1.81 |
| 120 | 54 | 43 | 38 | 56 | 44 | 45 | 1.04 | 1.02 | 1.18 |
| 20 | 847636 | 3457321 | 3997503 | 913065 | 3966638 | 2632852 | 1.08 | 1.15 | 0.66 |
| 40 | 225851 | 334451 | 467444 | 213491 | 400207 | 710068 | 0.95 | 1.20 | 1.52 |
| 60 | 12120 | 20465 | 31857 | 11830 | 27232 | 64480 | 0.98 | 1.33 | 2.02 |
| 80 | 1076 | 1576 | 2726 | 1069 | 2821 | 6162 | 1.01 | 1.23 | 1.86 |
| 100 | 34 | 29 | 27 | 35 | 30 | 28 | 1.03 | 1.03 | 1.04 |
| 20 | 2238714 | 3102375 | 2943019 | 1857368 | 3145357 | 2798119 | 0.83 | 3.01 | 0.95 |
| 40 | 116705 | 219415 | 276953 | 112073 | 245390 | 495529 | 0.96 | 1.12 | 1.79 |
| 60 | 5881 | 14436 | 17556 | 5785 | 15416 | 42808 | 0.98 | 1.07 | 2.44 |
| 80 | 549 | 1174 | 1358 | 552 | 1499 | 3411 | 1.01 | 1.28 | 2.51 |
| 100 | 87 | 111 | 101 | 89 | 144 | 247 | 1.02 | 1.30 | 2.45 |
| 120 | 21 | 18 | 16 | 22 | 19 | 17 | 1.05 | 1.06 | 1.06 |

### Table 2. Results for phase angle δ [°].

| T [°C] | 0% wax | 1.5% wax | 3.0% wax | 0% wax | 1.5% wax | 3.0% wax | 0% wax | 1.5% wax | 3.0% wax |
|-------|--------|----------|----------|--------|----------|----------|--------|----------|----------|
| TCP I (slow) | TCP II (fast) | δfast - δslow [°] |
| 20 | 48 | 36 | 33 | 59 | 34 | 20 | 11 | -2 | -13 |
| 40 | 60 | 56 | 53 | 61 | 57 | 52 | 1 | 1 | -1 |
| 60 | 72 | 67 | 63 | 73 | 69 | 61 | 1 | 2 | -2 |
| 80 | 82 | 77 | 69 | 83 | 75 | 61 | 1 | -2 | -8 |
| 100 | 88 | 83 | 78 | 88 | 83 | 69 | 0 | 0 | -9 |
| 120 | 90 | 89 | 90 | 90 | 90 | 87 | 0 | 1 | -3 |
| 20 | 54 | 40 | 39 | 52 | 51 | 38 | -2 | 11 | -1 |
| 40 | 66 | 61 | 57 | 67 | 62 | 55 | 1 | 1 | -2 |
| 60 | 77 | 69 | 65 | 78 | 71 | 58 | 1 | 2 | -7 |
| 80 | 85 | 80 | 65 | 85 | 72 | 57 | 0 | -8 | -8 |
| 100 | 89 | 85 | 80 | 90 | 83 | 69 | 1 | -2 | -11 |
| 120 | 90 | 90 | 90 | 90 | 90 | 86 | 0 | 0 | -4 |
| 20 | 54 | 45 | 47 | 54 | 43 | 33 | 0 | -2 | -14 |
| 40 | 69 | 61 | 60 | 71 | 64 | 56 | 2 | 3 | -4 |
| 60 | 80 | 67 | 68 | 81 | 70 | 58 | 1 | 3 | -10 |
| 80 | 87 | 76 | 71 | 87 | 71 | 59 | 0 | -5 | -12 |
| 100 | 90 | 85 | 86 | 90 | 82 | 69 | 0 | -3 | -17 |
| 120 | 90 | 90 | 90 | 90 | 90 | 90 | 0 | 0 | 0 |
In order to check for bias effects caused by binder sample flowing from the 1 mm gap during slow cooling time, softening point Ring and Ball was measured. The standard procedure for test sample preparation is uncontrolled cooling at room temperature which is significantly faster compared to site condition. For applying the slow cooling rate, the samples representing TCP I were cooled within a temperature-control cabinet. The resulting softening points are summarized in Table 3.
Table 3. Results for softening point ring and ball dependent of binder wax content.

| Wax content | 20/30 | 30/45 | 50/70 |
|-------------|-------|-------|-------|
| Normal cooling TCP II | 66,0 | 58,5 | 54,5 |
| Slow cooling TCP I | 78,5 | 68,0 | 75,0 |
| Slow cooling TCP I | 86,0 | 81,5 | 81,0 |

4. Discussion

As known from [3, 4] wax modification results in an increase of binder stiffness. Softening point ring and balls as well as rheological properties in a temperature range from 30°C to 100°C show increased complex modulus and an increase in elasticity which can be observed in a decrease of phase angle.

Figure 9 and Figure 10 show the measured phase angles after TCP I (slow cooling) and TCP II (fast cooling) for all binders with 0%, 1.5% and 3.0% wax modification. The phase angles obtained are spread wider after fast cooling (TCP II) indicating more distinct differences between the samples.

For the unmodified binders the phase angle increases continuously with increasing test temperature. For wax modified binders, the phase angle curve can be divided into three phases: Below the temperature of around 50°C, an increasing temperature results in increasing phase angle. Here the complex modulus of the bitumen is higher compared to the modulus of the wax itself and the phase angle is controlled by the properties of the neat bitumen. With further increasing temperatures up to approx. 70°C the temperature increase results in a phase angle decrease or a constant phase angle. This can be explained by the decreasing bitumen viscosity which results in increasing proportion of the wax properties within the overall sample properties resulting in increasing elasticity. With further increase of the temperature up to 110°C the wax network indicates decreasing stiffness at temperatures near its melting point which results again in an increase of phase angle.

Comparing phase angle development of unmodified and wax modified binders for TCP I in Figure 9, no characteristic phase progress produced by wax content in binder 20/30 can be recognized as described before. The results of δ are similar to unmodified binders. For binder 30/45 and 50/70 distinct wax characteristics can be observed.

Figure 10 shows results of δ for TCP II with wax characteristic for all modified binders. It should be noted that between test temperature 60°C and 90°C the influence of wax crystallization effect is less for binder 20/30 which results in higher phase angles with less elastic binder properties compared to 30/45 and 50/70. As a result, the influence in wax content is significantly stronger after TCP II compared to TCP I and binder viscosity influence wax ability forming crystal network.

Figure 9. Phase angle in TCP I (slow).

Figure 10. Phase angle in TCP II (fast).
After evaluation of the test results between TCP I and TCP II and with regard to the crystallised wax structure within all binders the hypothesis described in [1] has to be withdrawn. In [1] it was discussed that the sizes of the emerging crystals depend on the cooling rate and the viscosity of the material. In the results obtained it can be observed that a fast cooling rate results in more elastic properties than a slow cooling rate. That means that the wax crystal network within the bitumen resulting from fast cooling indicate higher stiffening effects compared to slow cooling rate.

With regard to the presented results of dynamic shear rheometer this structure is more sensitive to shear force as occurring within DSR tests and the measured results are similar to non wax modified binder sample.

The observations made within the DSR tests are confirmed by the softening points ring and ball. For the wax modified binders, the slow cooling results in differing values of \( T_{R&B} \). The difference between slowly and rapidly cooled samples is strongest for samples with 3 % wax addition.

5. Conclusions

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

- The cooling rate applied after casting (and trimming) specimen doesn’t affect the properties of the tested neat bitumen.
- The cooling rate affects the wax crystallization in FT-wax modified binders significantly. This results in systematically varying complex modulus, phase angle and also softening point. These differences has to be taken into account when comparing results of binder tests (usually measured on rapidly cooled samples) with laboratory asphalt mix properties in field conditions, for which slower cooling rates apply.
- The viscosity of the binder affects the wax crystallization. The differences between slow and fast cooled samples are highest for the 50/70 and lowest for the 20/30.
- In order to avoid wrong interpretation of bitumen tests, the cooling rate has to be taken into account for wax modified binders.

References

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