Assessing bitumen in the whole service-temperature-range with the dynamic shear rheometer

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ABSTRACT

During a research project in the years 2012 to 2014, 90 bitumens of different grades from eight different refineries were analyzed thoroughly. The results provide a detailed and extensive overview about the rheological properties and chem-ical compositions of the bitumens used in road construction in Germany.

The results, measured with the Dynamic Shear Rheometer (DSR) at cold temperatures, correspond well with the stiff-ness and the relaxation-properties, measured with the Bending Beam Rheometer. The stiffness at 25 °C corresponds well with the needle penetration at the same temperature. The improvements of the DSR-analysis at this temperature are a better differentiation of harder bitumens and the additional information, given by the phase angle. The properties at high service temperatures could also be analyzed more precisely and more performance related with the DSR. Un-modified bitumens show a precise correlation between the stiffness and the softening point ring and ball. Due to the fact that the determination of the softening point of modified bitumens often causes problems, an equiviscosity tem-perature for the shear modulus of 15 kPa is a suitable substitute for the softening point ring and ball. For the very rea-son that the viscosity at high temperatures is a suitable criterion for the asphalt's production, processing and compac-tion, the DSR gives an analysis of the bitumen's whole service-temperature-range.

The results of the research project show that all currently used test methods can be replaced equivalently by the DSR. Furthermore, the DSR provides characteristic values for a more precise bitumen analysis, particularly for modified bitumens.

Keywords: Performance testing, Physical properties, Rheology, Stiffness, Testing

1. INTRODUCTION

In the research project "Influence of Bitumen Properties on the Adhesion Behaviour of different Aggregates" [1] a representative cross section of the bitumens, being inserted during the construction seasons 2012 and 2013 in Germany, was analyzed chemically and physically. A result of the research is an overview of the average physical characteristics and chemical compositions as well as the uniformity of paving grade bitumen being used in Germany. Furthermore, based on different physical test methods the research allowed a comparison between conventional test methods and characteristics of the Dynamic Shear Rheometer (DSR).

2. TEST PROGRAM

90 paving grade bitumens, which were produced in eight different refineries throughout Germany, and six polymer modified bitumens were sampled in total. For each paving grade bitumen of each refinery one sample was provided directly by the particular refinery. Any other bitumen samples were immediately taken out of the daily business in the mixing plants over a time period of two years. Hereby, it was ensured that the samples comply with the bitumens, which are actually used in asphalt road construction in Germany.

The 90 paving grade bitumens include the grades 20/30, 30/45, 50/70, 70/100 and 160/220. In accordance with their frequency of use in asphalt road construction, bitumens 50/70 and 70/100 constituted a majority of the test program (57 out of 90 samples). The other 33 samples spread over the remaining grades. It is to mention that grades 20/30 and 30/45 could not be obtained from all refineries because they were not produced in all refineries.

For the sampling, eight refineries throughout Germany, which produce a significant amount of the bitumen that is used for German road construction, were selected. The refineries are located in (see figure 1):

- Brunsbüttel
- Gelsenkirchen
- Heide
- Karlsruhe
- Köln
- Leuna
- Schwedt
- Vohburg

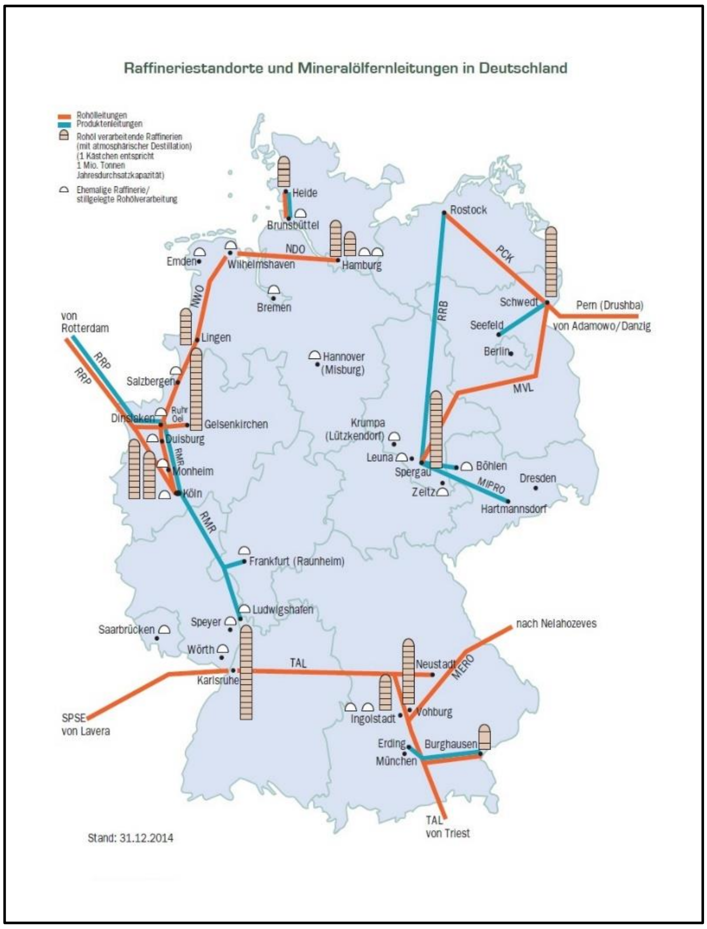


Figure 1: Refinery location and pipelines in Germany [2]

Besides the sampling of 90 paving grade bitumens, modifications with each three different elastomers and plastomers were performed. The modifications were conducted with the object of analyzing the general impact to the bitumen's rheological properties.
The following physical parameters were determined for all bitumen samples in fresh state and after short term aging (RTFOT according to EN 12607-1):

- Needle penetration at 25 °C according to EN 1426
- Softening point ring and ball according to EN 1427
- Fraaß breaking point according to EN 12593 (not after RTFOT)
- Flexural creep stiffness and m-value according to EN 14771 (not after RTFOT)
- Complex shear modulus and phase angle according to EN 14770

The characteristic values of flexural creep stiffness and m-value were determined by Bending Beam Rheometer (BBR) uniformly at a temperature of -16 °C after a loading duration of 60 seconds.
With the Dynamic Shear Rheometer (DSR) the stiffness (complex shear modulus) and the elastic resp. plastic deformation potential (phase angle) were determined for the entire temperature range that is relevant for asphalt road construction. The temperature range from -10 to + 150 °C was selected with intervals of 10 °C. The test parameters are summarized in the following table 1.

Table 1: Test parameters for the determination of complex shear modulus and phase angle (DSR)

Measuring system	plate / plate
Type of testing	position-controlled / oscillating
Given deformation	0,1 to 10 %
Test temperature range	-10 to +150 °C
Test interval	10 °C
Test frequency	1,59 Hz
Sample diameter	8 mm resp. 25 mm
Gap width	2 mm resp. 1 mm

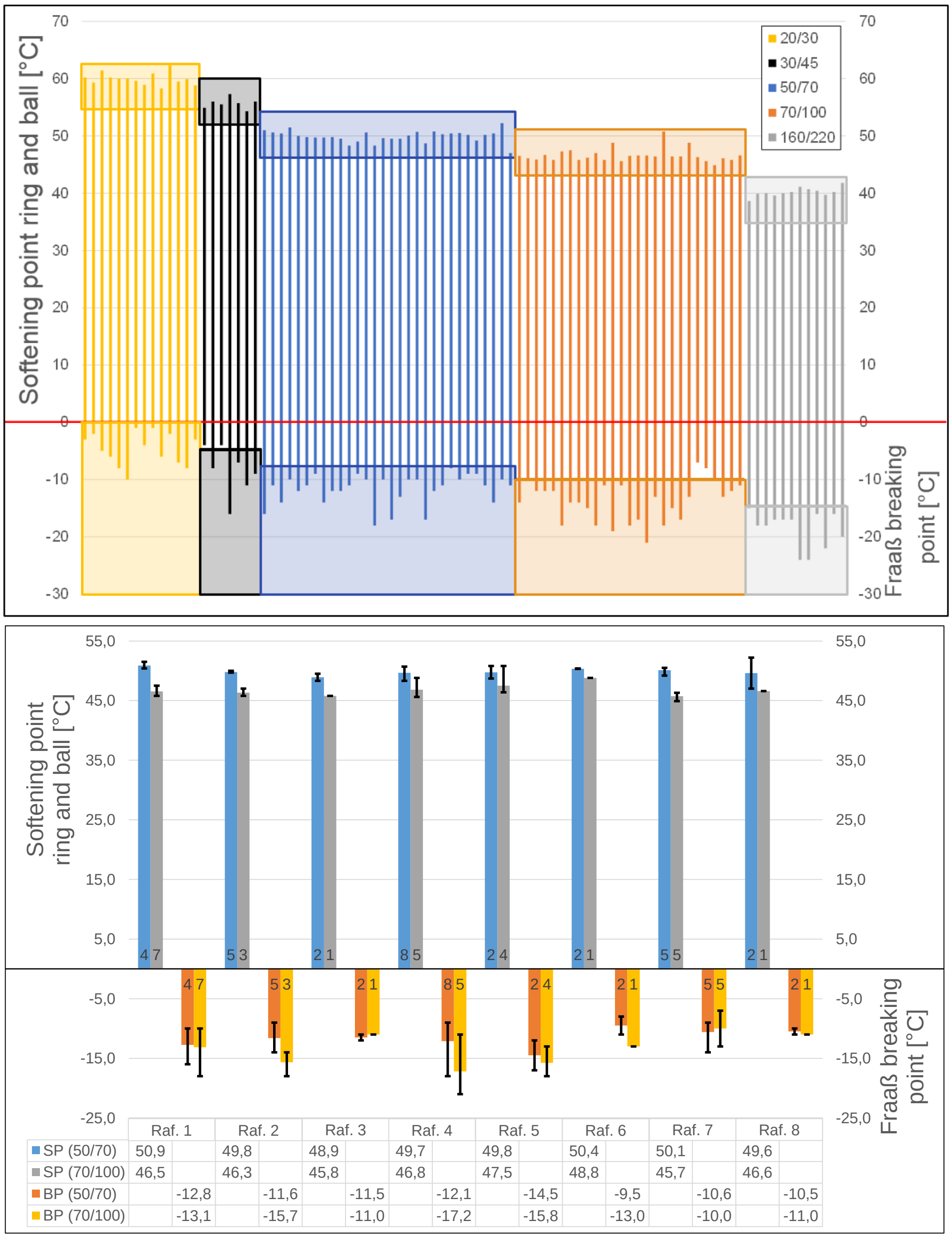
All fresh paving grade bitumens were analyzed chemically as follows:

- SARA-analysis according to SEBOR [3]
- Dividing asphaltenes into easy, medium and difficult soluble compounds according to ZENKE [4]
- Distilling analysis according to THIMM [5]

The principle of SARA-analysis is primarily based on the polarity of the different fractions of the bitumen. For the SARA-analysis, bitumen is separated in the fractions of aliphatic compounds, mono-, di- and poly-aromatics and polar compounds by column chromatography after severing of the asphaltenes.
For the division of asphaltenes according to ZENKE, asphaltenes are severed by repeated dissolving and precipitating into its easy, medium and difficult soluble compounds.
The distilling analysis is implemented by a gas chromatography. Thereby, bitumen is warmed up continuously in a pillar. The analysis starts at 45 °C with a temperature gradient of 7.5 °C/min. The analysis ends at constant temperature of 430 °C, held for a period of 30 minutes. A detector collects the proportion, which distills in dependency of the temperature. Because smaller carbon compounds distill earlier than bigger, conclusions on the compound of chemical bonds of the bitumen can be drawn by its distilling behavior.

3. EXPERIMENTAL RESULTS

All analyzed paving grade bitumens fulfil the requirements for the softening point ring and ball according to TL Bitumen-StB 07/13, the German implementation of EN 12591 and EN 14023 (figure 2, top). 82 of the 90 examined bitumens even show a softening point ring and ball, whose deviation from the average of the particular bitumen type is less than 2 °C, despite a given range of 8 °C.
The Fraaß breaking points also fulfil, with only three exceptions, reliably the requirements according to TL Bitumen-StB 07/13 (figure 2, top). On average, the measured values are 3.7 °C below the maximum breaking points. But the dispersion of the breaking points is far bigger than the dispersion of the softening points ring and ball. This does not only apply to bitumens of the same grade, but also to bitumens of the same grade that come from the same refinery as well (see figure 2, down). So, the dispersion of breaking points of bitumens 50/70 from the same refinery is 4.4 °C on average while the softening points ring and ball of bitumens 50/70 from the same refineries only have dispersions of 1.7 °C on average.



	Raf. 1		Raf. 2		Raf. 3		Raf. 4		Raf. 5		Raf. 6		Raf. 7		Raf. 8	
SP (50/70)	50,9		49,8		48,9		49,7		49,8		50,4		50,1		49,6	
SP (70/100)	46,5		46,3		45,8		46,8		47,5		48,8		45,7		46,6	
BP (50/70)		-12,8		-11,6		-11,5		-12,1		-14,5		-9,5		-10,6		-10,5
BP (70/100)		-13,1		-15,7		-11,0		-17,2		-15,8		-13,0		-10,0		-11,0

Figure 2: Softening point ring and ball resp. Fraaß breaking point; top: all analyzed paving grad bitumens; down: average values and spread of bitumens 50/70 and 70/100, each depending on the refinery

The complex shear modules and phase angles show minor differences between bitumens of the same grade. This, in particular, applies to bitumens of the same grade that come from the same refinery. According to the softening points ring and ball, these minor differences were determined especially in the middle temperature range. Figure 3 shows that there are almost no distinctions between the complex shear modules resp. phase angels of bitumens of the same grade between 30 and 90 °C – i.e. in the temperature range, in which bitumens have to be examined with the DSR according to TL Bitumen-StB 07/13. At lower temperatures the clear distinction between bitumens of different grades decreases. Compared to the conventional test results Fraaß breaking point and softening point ring and ball, dispersions of the results of bitumens of the same type at a higher temperature range are lower than at a lower temperature range. This high fluctuation in bitumen's cold temperature properties are also shown in the results of the BBR-examination that are not presented in this article (see [1]).

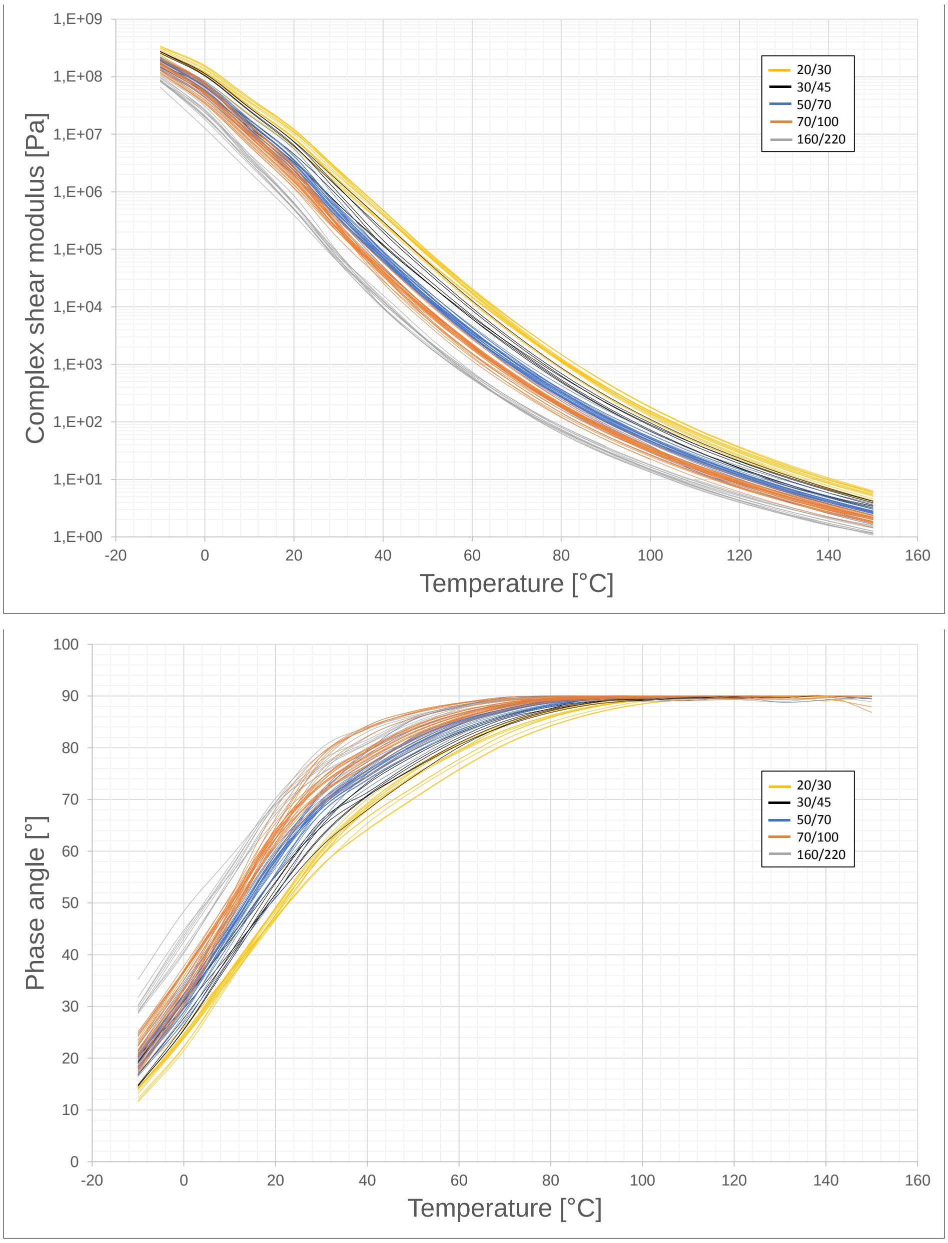
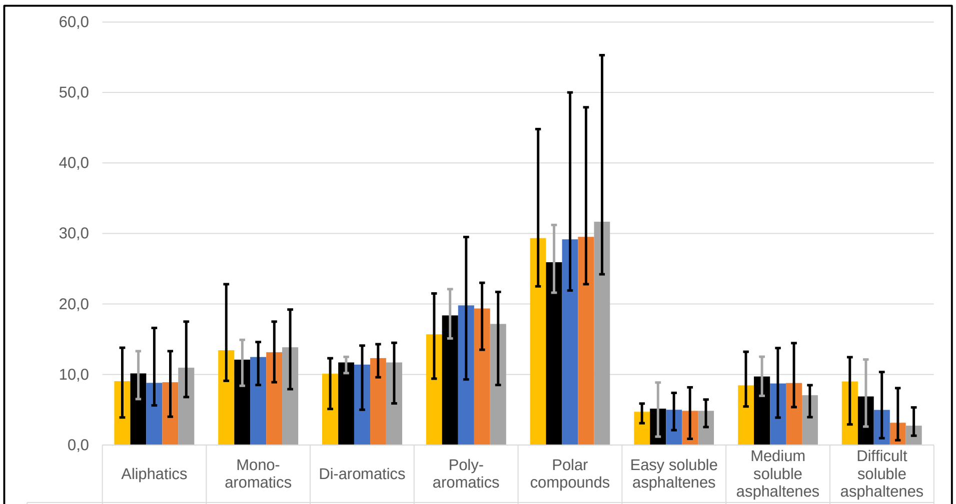


Figure 3: Temperature dependent complex shear modules (top) and phase angles (down) of the analyzed paving grade bitumens

While the physical characteristics are likely to be minor, the chemical examinations show large differences between bitumens of the same grade and also between bitumens of the same grade that come from the same refinery. The dispersion of bitumens of the same grade are significantly higher than the – partly not even existing – differences between the different bitumen grades. Only the amounts of asphaltenes – especially the amounts of difficult soluble asphaltenes – show a distinct tendency to decrease for softer bitumen grades. Even here, the dispersions in the case of bitumens of the same grade are much larger than the dispersions between the different grades of bitumen (see figure 4, top).
Even bitumens of the same grade, which come from the same refinery in each case, show no consistent composition. This is shown in figure 4 (down) exemplarily for bitumens 50/70 of the eight different refineries.



	Aliphatics	Mono-aromatics	Di-aromatics	Poly-aromatics	Polar compounds	Easy soluble asphaltenes	Medium soluble asphaltenes	Difficult soluble asphaltenes
20/30	9,1	13,4	10,1	15,7	29,3	4,7	8,5	9,0
30/45	10,1	12,1	11,7	18,4	25,9	5,1	9,7	6,9
50/70	8,8	12,5	11,4	19,8	29,2	5,0	8,7	5,0
70/100	8,9	13,2	12,3	19,4	29,5	4,8	8,8	3,2
160/220	11,0	13,9	11,7	17,2	31,7	4,8	7,1	2,7

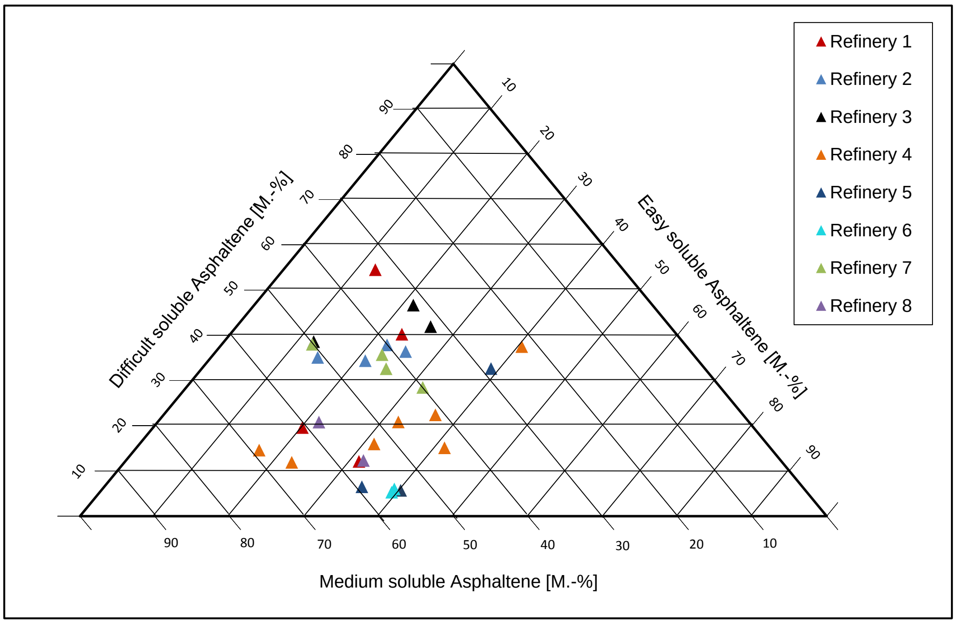


Figure 4: SARA-analysis and separation into easy, medium and difficult soluble asphaltenes; for every bitumen grade the average value as well as the minimum and the maximum (top); ternary plot for easy, medium and difficult soluble asphaltenes of bitumens 50/70 form different refineries (down)

Even the distilling analysis shows no correlation to the bitumen's stiffness resp. the bitumen grade. Figure 5 illustrates that the chemical composition does not show a characteristic behavior. Hence, in contrast to the rheological properties (cf. figure 3 with significant divided values for each bitumen grade), the chemical composition shows no substantial relationship to the bitumen's physical properties.

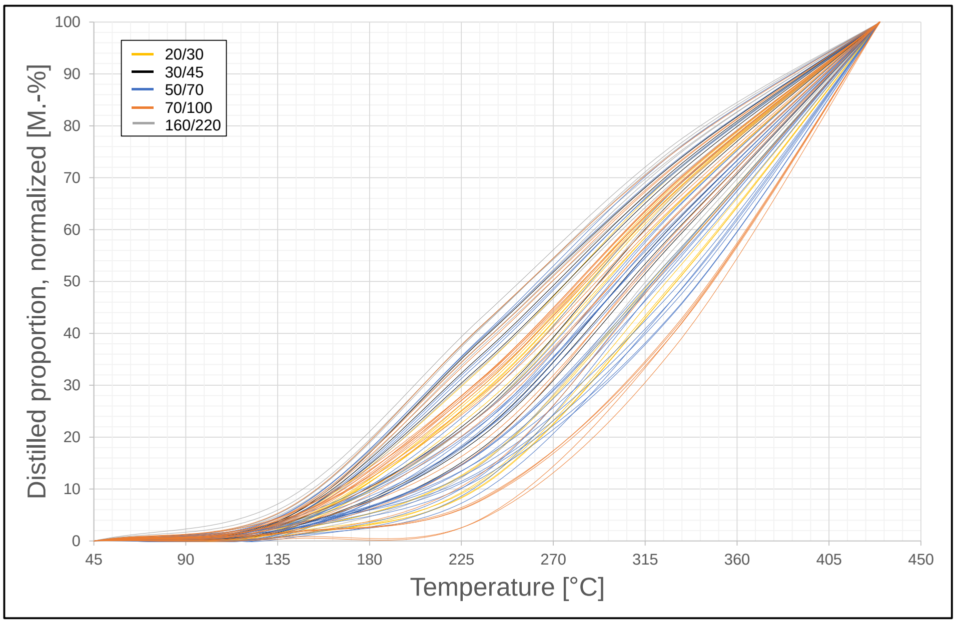


Figure 5: Results of the distilling analysis

4. INFLUENCE OF CHEMICAL COMPOSITION ON PHYSICAL CHARACTERISTICS

As already shown by the comparison of figure 3 (rheological properties show minor differences between bitumens of the same grade) and figure 5 (distilling analysis shows no dependency on the bitumen grade), no direct correlation between distilling behavior and physical characteristics can be determined. The composition of the maltene phases (aliphates, aromatic compounds and polar compounds) also shows no correlation to the physical characteristics (cf. figure 4). Only the asphaltene content correlates with bitumen's stiffness. As shown in figure 6, using the example of the correlation between asphaltene content and softening point ring and ball, the 90 analyzed paving grade bitumens show that bitumen's stiffness increases with an increasing asphaltene content. The correlation coefficients of 0.62 shows the mentioned trend, but an exact correlation between the bitumen's stiffness and the chemical composition cannot be determined.

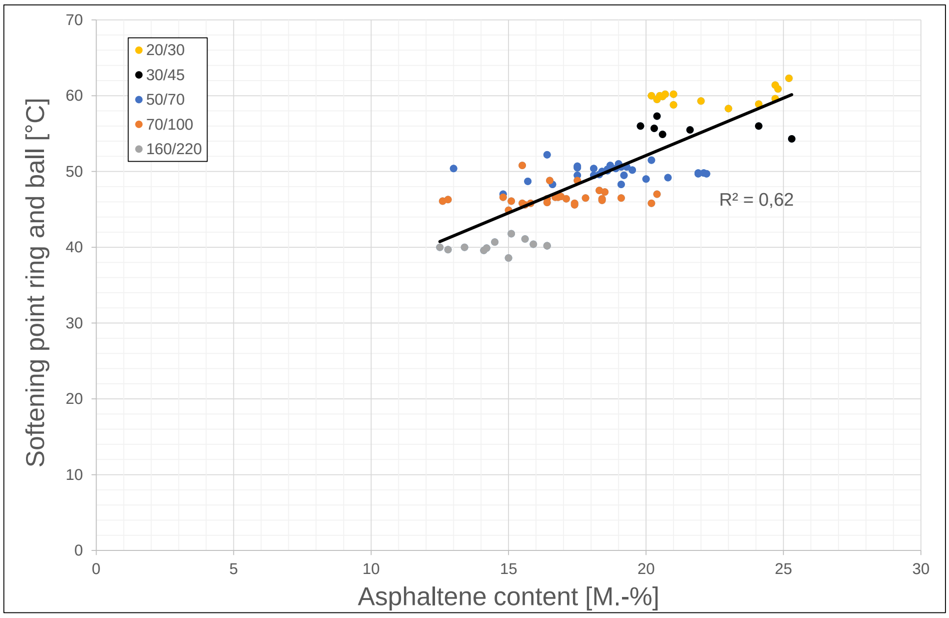


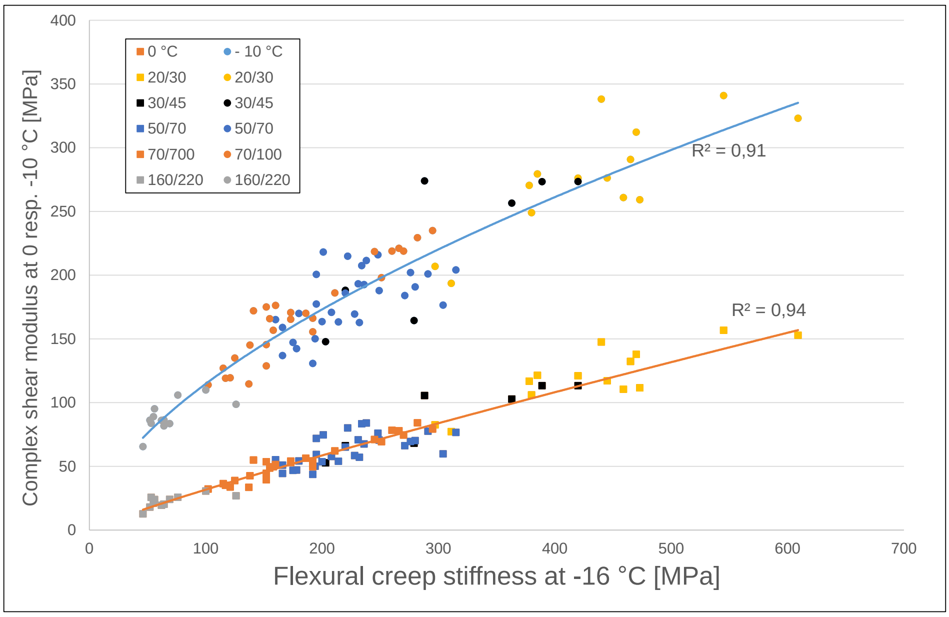
Figure 6: Correlation between asphaltene content and softening point ring and ball

5. RELATIONSHIP BETWEEN CONVENTIONAL AND RHEOLOGICAL (DSR) TEST RESULTS

According to European standards the requirements regarding the physical characteristics of bitumen are still formulated by conventional test results: Fraaß breaking point, needle penetration at 25 °C and softening point ring and ball. Due to the fact that the quite common DSR provides reliable and precise results, the equivalence between complex shear modulus resp. phase angle and conventional test results were examined. With 90 paving grade bitumens, a broad basis of the bitumens used in Germany served for this.

5.1 Low temperature properties

While the low temperature properties are assessed differently by Fraaß breaking point and the BBR test results (see [1]), the stiffness measured with BBR and DSR are comparable (figure 7, top). At measuring temperatures of 0 resp. -10 °C, where characteristic complex shear modules can be determined, with correlation coefficients higher 0.9, direct correlations between complex shear modulus and flexural creep stiffness (BBR) at -16 °C exist.



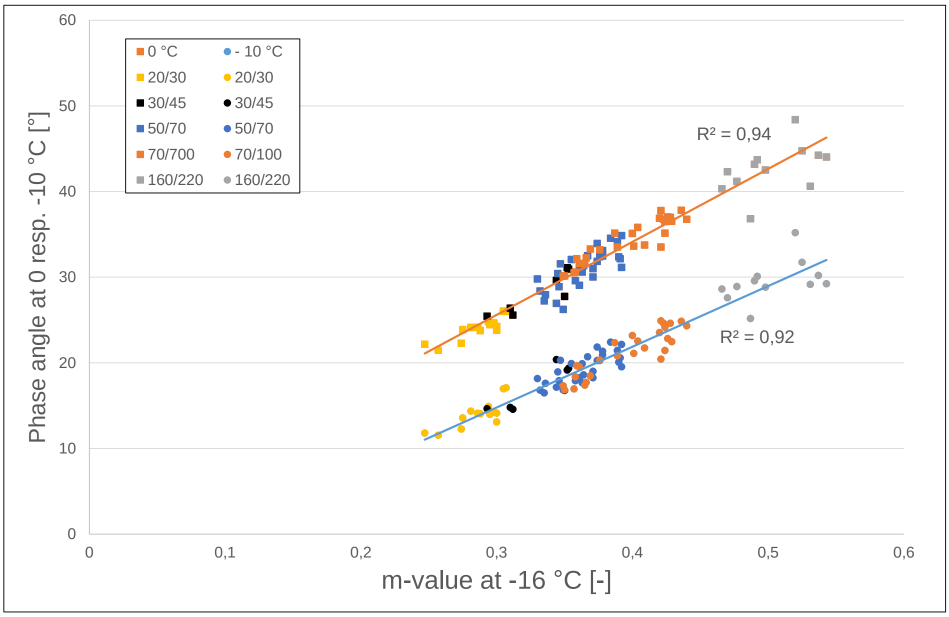


Figure 7: Correlation between BBR results at -16 °C and DSR results at 0 resp. -10 °C; top: flexural creep stiffness of complex shear modulus; down: m-value of phase angle

Especially at low temperatures, paving grade bitumens show direct correlations between complex shear modulus and phase angle as well as between flexural creep stiffness and m-value (see [1]). With correlation coefficients higher 0.92, precise correlations between m-value (BBR) and phase angle (DSR) exist at the temperatures mentioned above (figure 7, down). This is mainly due to the fact that stiffness and relaxation behavior correlate well for paving grade bitumens: increasing stiffness causes deteriorating relaxation properties.

5.2 Service temperature properties

The service temperature behavior is conventionally characterized by the needle penetration at 25 °C. This method especially shows weaknesses with the increasing use of modified bitumens and with hard bitumens differing by only a few tenths of a millimeter. These weaknesses can theoretically be eliminated by the replacement of the needle penetration with the DSR – so the complex shear modulus at 25 °C. Figure 8 shows a correlation coefficient of 0.93, which shows that the complex shear modulus and the needle penetration – each at 25 °C – provide equivalent results. In other words, the DSR delivers an adequate replacement for unmodified bitumens, for which the needle penetration presents a reliable characteristic, and a better replacement for modified or hard bitumens. A confirmed improvement for the modified bitumen's analysis applies for the phase angle. In contrast to paving grade bitumen (direct correlation between needle penetration and phase angle, see figure 8), the phase angle provides a separate parameter for modified bitumens.

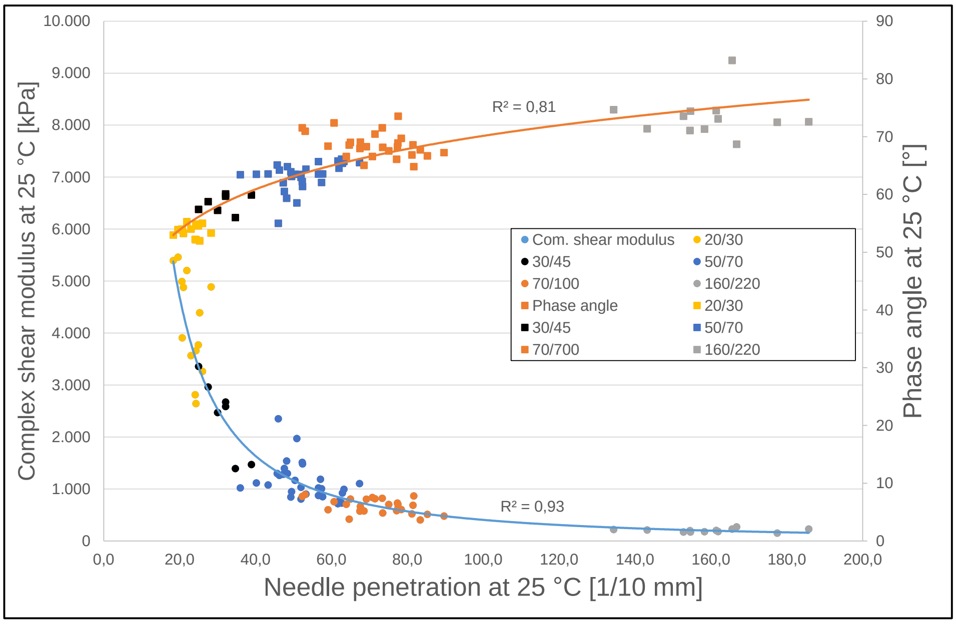
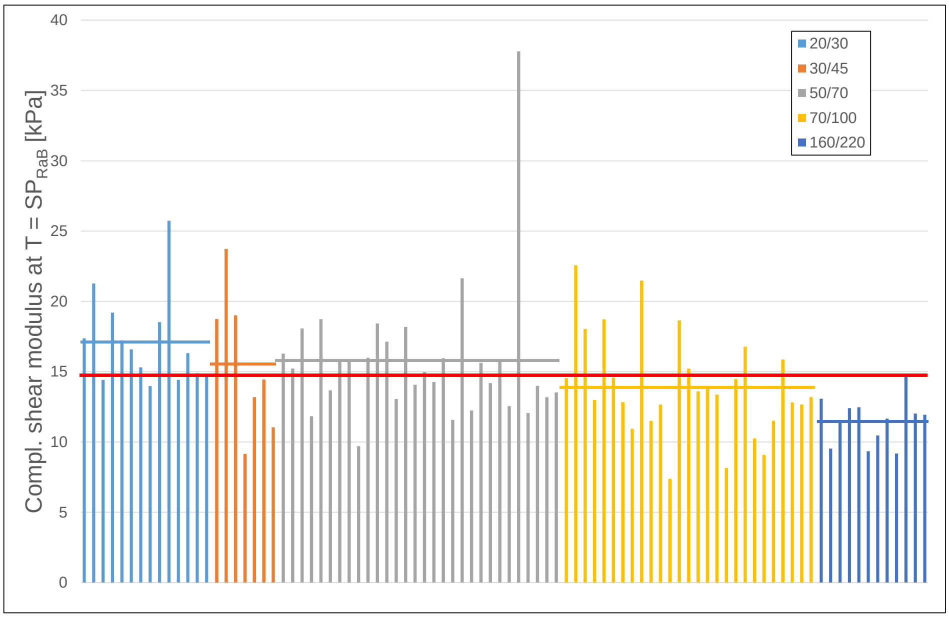


Figure 8: Correlation between needle penetration and complex shear modulus resp. phase angle (each at 25 °C)

5.3 Properties at high service and processing temperature

Besides measuring problems in the needle penetration, in some cases measuring problems also exist by the determination of softening point ring and ball of modified bitumens. Therefore, an equiviscous temperature was defined on the broad basis of 90 unmodified bitumens, which were analyzed during the research project. For this, the complex shear modules were determined, which were measured at the temperature of the softening point ring and ball. At a tendential decrease of the complex shear modulus with increasing bitumen stiffness, this complex shear modulus at the temperature of the softening point ring and ball is 14.85 kPa in average – so approximately 15 kPa (figure 9, top).
A comparison of the defined equiviscous temperature $EG^*_{15kPa}T$ shows a good correlation with the softening point ring and ball. For the 90 analyzed paving grad bitumens the correlation coefficients is 0.94 (figure 9, down).
Based on the equiviscous temperature $EG^*_{15kPa}T$, alternative limits for the bitumen's high service temperature properties can be recommended to replace the softening point ring and ball. By setting a temperature range of 5 °C around the average $EG^*_{15kPa}T$ for each bitumen grade, the appropriate limits of table 2 are defined. The chosen temperature ranges are defined more precisely than the softening points ring and ball (8 °C for each bitumen grade in TL Bitumen-StB 07/13). Furthermore, in contrast to the softening point ring and ball this definition provides a clear separation between the different bitumen grades (figure 10, top). In spite of that, only 6 of 90 analyzed bitumen do not meet the requirements.



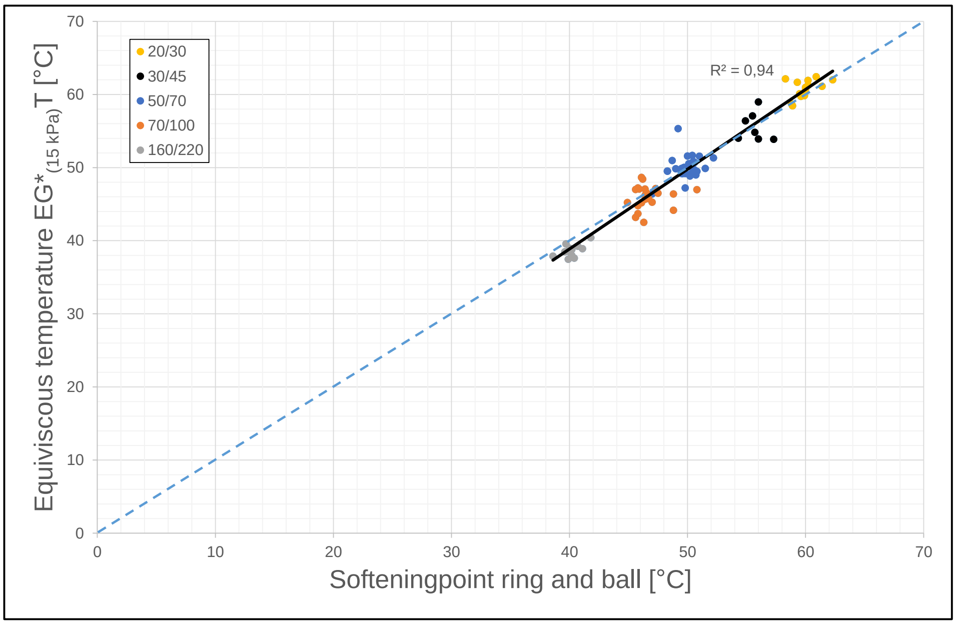
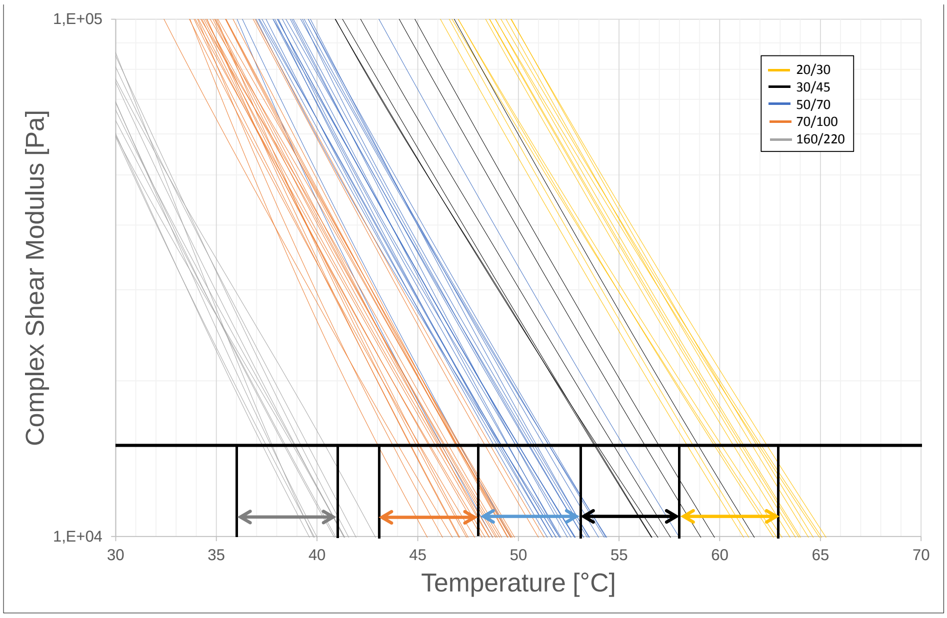


Figure 9: Complex shear modulus at the temperature of the softening point ring and ball (top); correlation between softening point ring and ball and equiviscous temperature EG*$_{15kPa}$T (down)

Table 2: Average, minimum and maximum EG*$_{15kPa}$T and appropriate limits for each bitumen grade

Bitumen grade	Average EG*$_{15kPa}$T	Minimum EG*$_{15kPa}$T	Maximum EG*$_{15kPa}$T	Appropriate limits
36 – 41	60,8	58,4	62,1	58 – 63
43 – 48	55,6	53,9	59,0	53 – 58
48 – 53	50,0	46,4	55,3	48 – 53
53 – 58	45,9	42,5	48,7	43 – 48
58 – 63	38,6	37,5	40,4	36 – 41



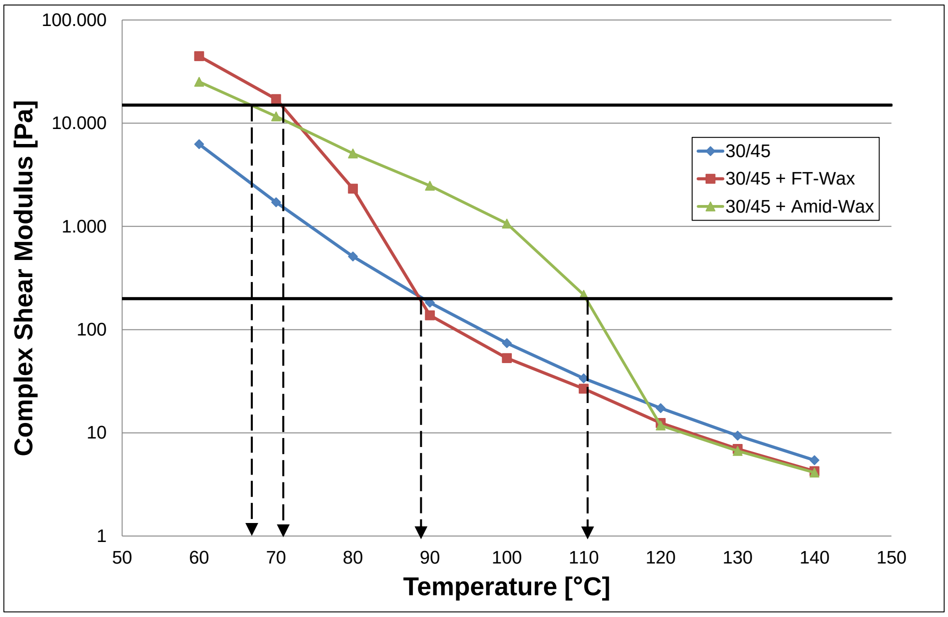


Figure 10: Recommended limits of EG*$_{15kPa}$T for each bitumen grade (top); identification of wax-modified bitumens by EG*$_{15kPa}$T and EG*$_{0,2kPa}$T (down)

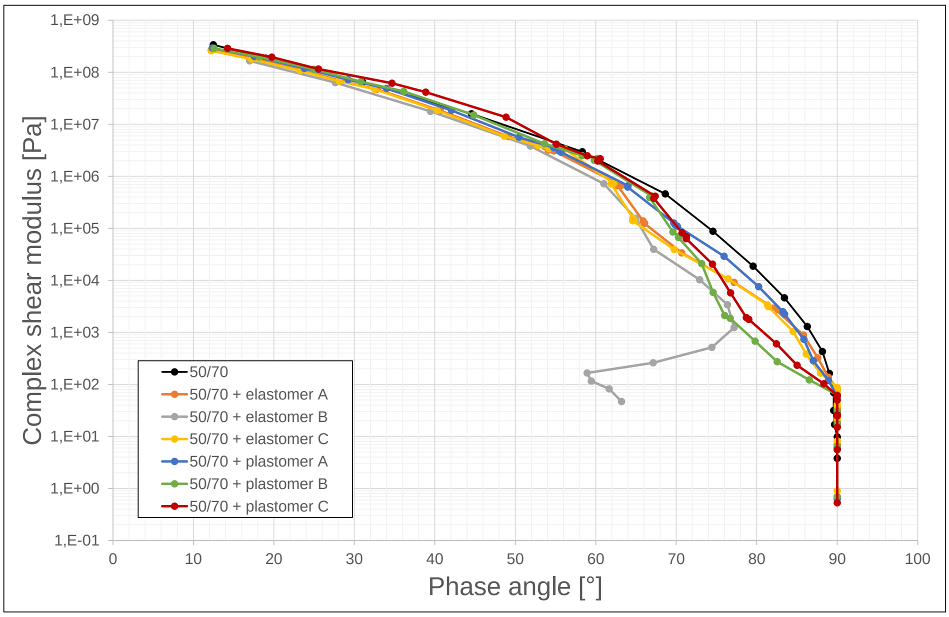
Because such equiviscous temperatures allow a more precise bitumen characterization especially for modified bitumen (cf. [6]), requirements for the classification of wax-modified bitumens are under discussion in Germany. Besides EG*$_{15kPa}$T as a more performance related replacement for softening point ring and ball, a second equiviscous temperature enables us to identify the type of wax. On the basis of the equiviscous temperature EG*$_{0.2kPa}$T, meaning the temperature at which the complex shear modulus is 0.2 kPa, the different types of waxes (Fisher-Tropsh-Wax or the like resp. Amid-Wax or the like) can be distinguished. By measuring the complex shear modulus under decreasing temperature, the equiviscous temperature EG*$_{0,2kPa}$T for the first-mentioned group of waxes is about 90 °C and for the other group of waxes about 110 °C (figure 10, down). Due to the strong effect of the waxes, the mentioned temperatures are almost independent of the base bitumen.

Within the temperature ranges of the asphalt production and processing the analyses by DSR are recognized for a number of years. Measurements using a DSR in rotation mode according to DIN EN 13702-1 deliver a dynamic viscosity as a result, which is distinctive for the asphalt's properties at production and processing temperature.

5.4 Characteristic properties over the entire temperature range

The executions in sections 5.1 to 5.3 show that measurements with the DSR can equivalently replace classical test results with paving grade bitumens in all temperature ranges.

Furthermore, the rheological behavior in general can be assessed by the DSR-measurements. This illustrates figure 11 on the basis of the black-diagram showing the influence of polymer modifications resp. of aging. In figure 11 (top) it can be seen, that different polymer additives each show a characteristic shift of the function course (complex shear modulus depending on the phase angle) especially at phase angels of 50 to 90 °. A short time aging causes a shift up to lower phase angles with the same complex shear modulus in almost the same range. The phase angles with regard to the complex shear modulus of 1 MPa decline mostly independent of the bitumen stiffness and provenance by approximately 8 ° on average (figure 11, down).



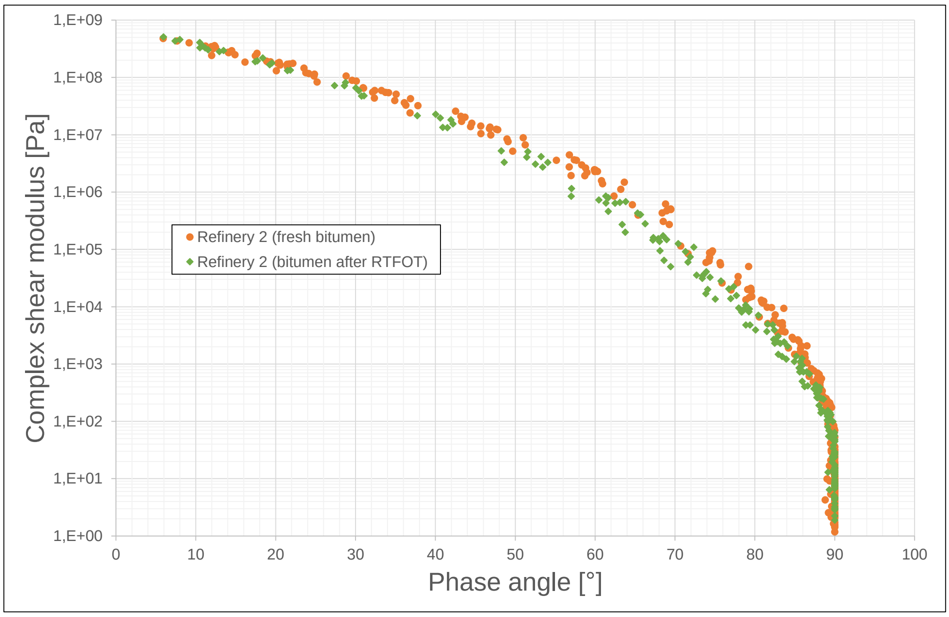


Figure 11: top: Black-diagram of a bitumen 50/70 before resp. after modification with different polymers; down: Black-diagram of identical bitumens before and after short time aging (RTFOT)

6. CONCLUSIONS

Paving grade bitumen used in Germany meets the placed requirements of TL Bitumen-StB 07/13 very precisely. With few expectations, at higher service temperature ranges only minor differences occur between bitumens of the same grade. This applies in particular to bitumens of the same grade, which also come from the same refinery. Although the physical properties comply with the given limits of TL Bitumen-StB 07/13, considerably large fluctuations can be determined in the cold temperature range. This general conclusion can be drawn on the basis of the conventional test results as well as on the basis of the rheological analyses.
The analyzed paving grade bitumens show a significantly large dispersion in chemical composition. This applies to bitumens of the same grade and – in minor form – to bitumens of the same refinery. Apart from the general trend, that

harder bitumens show higher asphaltene contents than softer bitumens, no characteristic correlations between the physical characteristics and the chemical compositions are discovered.

Analyzing 90 paving grade bitumens, rheological test results of the DSR-measurements provide a nearly identical bitumen characterization at corresponding temperatures just like in the conventional test results, what confirms the results of Eurobitume TF Data Collection [7] principally:

- In cold temperature ranges, flexural creep stiffness and m-value correlate well with complex shear modulus and phase angle.
- Complex shear modulus and needle penetration – each at 25 °C – describe the bitumen properties nearly the same. Furthermore, the complex shear modulus provides a more precise result especially for hard bitumens and the phase angle constitutes another significant parameter in the service temperature range especially for modified bitumens.
- The softening point ring and ball can be replaced by the equiviscous temperature $EG^*_{15kPa}T$, so the temperature at which the complex shear modulus is 15 kPa. For paving grade bitumens, this equiviscous temperature corresponds to the softening point ring and ball. Based on the research project's results, the bitumen grades can be specified more precisely by the equiviscous temperature $EG^*_{15kPa}T$. Furthermore, modifications like waxes can be determined more precisely and exact, performance related requirements can be formulated.

Besides the aforementioned points, the rheological behavior of the bitumen can be gathered by the DSR results in general. For example, by the presentation in a black-diagram, modifications or binder aging show a characteristic behavior. In summary, it can be said that the DSR enables us to replace the conventional tests. It is equivalent resp. even better in many cases due to more performance related, more precise and physically exact defined results with only one test method.

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