Bitumen as required – the dream of a designed binder

Sandra Weigel[1, a], Dietmar Stephan[1, b]

[1] *Field Building Materials and Construction Chemistry, Technische Universität Berlin, Berlin, Germany*

[a] sandra.weigel@tu-berlin.de
[b] stephan@tu-berlin.de

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ABSTRACT

The objective of this work is to bring rheological and chemical properties of the bitumen together. As rheological investigation methods, the determination of the softening point (Ring and Ball method) as well as the determination of the complex shear modulus |G| and the phase angle δ with the Dynamic Shear Rheometer were carried out. As chemical analyses, the separation of asphaltenes to determine the asphaltene content, the further separation of the maltene phase using column chromatography to determine the content of the saturates, aromatics and resins and the gel permeation chromatography to determine the molecular weight were carried out. The relationships between the rheological and chemical parameters were investigated by multiple regression analyses.*

It shows inter alia that the viscosity and the stiffness of the bitumen are dependent on both the asphaltenes and the maltene fractions. In contrast, the deformation behaviour of the bitumen is mainly determined by the asphaltene content.

Furthermore, the contents and molecular weights of the SARA fractions provide information about the sensitivity of ageing and the bitumen behaviour after ageing. The findings can be of benefit for the selection of an appropriate binder for road construction and for the recycling of bitumen.

Keywords: Ageing, Chemical properties, Modified Binders, Rheology

1. INTRODUCTION

In Germany the road network consists to 95% of asphalt [1] whereat the number of damaged road surface and potholes increases in recent years. One significant factor to the conditions of the road surface is the binder bitumen which changes its properties especially as a result of ageing. Thereby, the properties of the bitumen, not only the sensitivity of ageing, are depending on the chemistry of the binder. Nevertheless, in practice principal rheological and physical test methods are carried out to characterize the bitumen while the chemical features are not taken into account.
But precisely because of chemical characteristics having such a significant effect on the rheological behaviour of the binder, different chemical investigations of various pavement bitumen were carried out within the scope of a BASt project (Bundesanstalt für Straßenwesen – Federal Highway Research Institute). The aim of this project is to find relationships and dependencies between the chemistry and rheology of the binder and to improve the possibility to predict the rheological and ageing behaviour due to chemical properties of the bitumen. Also the development of a binder design will be aimed in the project as a sublime vision. This binder design should allow the arrangement of *ideal bitumen* for any demands.

2. OVERVIEW OF THE CHEMISTRY OF BITUMEN

Bitumen is an organic binder consisting of a huge number of hydrocarbon compounds with several functional groups of sulfur, oxygen and nitrogen [2]. Because of the huge number the compounds are not separately identifiable, and are instead summarized in different fractions. These are the so called SARA fractions including the **s**aturates, **a**romatics, **r**esins and **a**sphaltenes [2]. In general, the saturates, aromatics and resins are summarized as maltenes which differ from the asphaltenes due to their solubility in n-heptane. The individual fractions of the maltenes are separated due to various polarities [3]. Concerning the structure of the different fractions, the polarity, aromaticity and the molecular weight increase steadily from saturates to aromatics to resins to asphaltenes [2, 4] demonstrating in Figure 1.

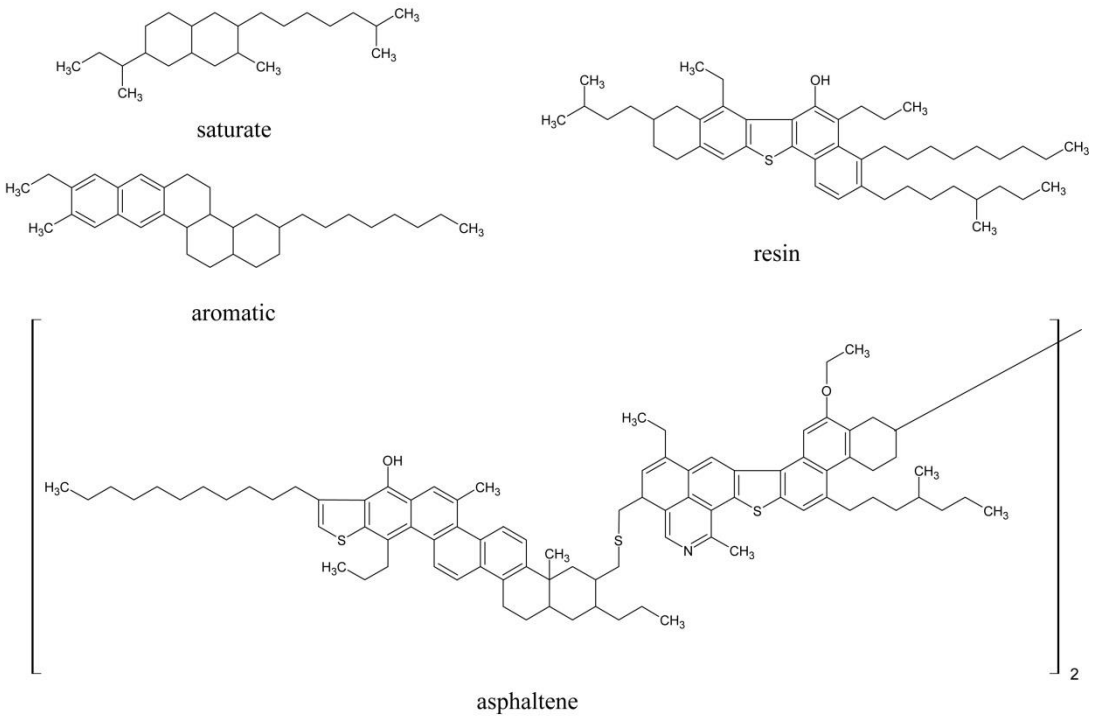

Figure 1 Exemplary presentation for the molecular structures of the SARA fractions (following [5])

It is known from the literature that the asphaltenes have a significant influence on the rheological bitumen properties. Thereby, an increasing content of asphaltenes results in an increasing hardness and viscosity [2] and shows an influence of the sensitivity of ageing [7].

3. MATERIALS AND METHODS

In order to reach the objectives and find relationships between the rheological and chemical properties, several bitumen samples were investigated with various rheological and chemical methods.

3.1 Materials

In this project, 11 bitumen samples with different viscosity were tested belonging to the grades 20/30, 30/45, 50/70 and 70/100. In addition, the samples originate from various refineries to cover as most different proveniences of the crude oils as possible (Table 1).

Table 1: Overview of the used bitumen samples

Refinery \ Grade	20/30	30/45	50/70	70/100
A	x	x	x	x
B			x	x
C		x		
D			x	x
E	x	x		

The original bitumen samples were aged with short term and long term ageing simulation. The short term ageing was conducted by the *Rotating Flask Test (RFT)* in accordance with DIN EN 12607-3 and the long term ageing by an additional ageing with the *PAV* (*Pressure Ageing Vessel*) in accordance with DIN EN 14769.

3.2 Methods

In order to evaluate the rheological properties of the bitumen samples, the determination of the *softening point* $t_{R\&B}$ in accordance with DIN EN 1427 (Ring and Ball method) was carried out as a conventional method. The softening point describes the temperature at a defined viscosity of the bitumen, and thus characterizes the viscosity at higher temperatures [8]. Furthermore, the investigation with the *Dynamic Shear Rheometer* (*DSR*) following DIN EN 14770 and TL Bitumen StB 07 was made as performance-related specification. The measuring geometry was a plate-plate-system with diameters of 8 and 25 mm using a deformation of 0.5% and a frequency of 1.59 Hz. For the following evaluation, the *complex shear modulus* $|G^*|$ and the *phase angle* δ at 50°C are considered. Thereby, the complex shear modulus $|G^*|$ represents a measure for the total resistance of the bitumen against deformations, in other words the stiffness, whereas the phase angle δ describes the ratio between the elastic and plastic deformation component, in other words the deformation behaviour [9, 10].

Concerning the chemical investigations of the bitumen samples, first, the separation of asphaltenes was carried out following the DIN 51595 and using n-heptane whereby the maltenes were collected for further studies. Thus, the maltenes were separated in the five fractions of the saturates, monoaromatics, diaromatics, polyaromatics and polar aromatic compounds (resins) using the liquid adsorption chromatography (column chromatography) following Šebor et al. [11]. After separation the content of the individual fractions was determined. For better clarity, the content of monoaromatics, diaromatics and polyaromatics were combined to the total aromatics. For the column chromatography, aluminium oxide and silica gel were used as stationary phase. As mobile phase hexane, a mixture of hexane and toluene in the ratios of 24:1 and 22:3, pure toluene and a mixture of toluene, diethyl ether and methanol in a ratio of 1:1:3 were used. For the asphaltene and maltene separation a duplicate determination was carried out whereby the average variation coefficient of the different fraction assumed a value of 4.9 wt.%.

Finally, both the original bitumen and the individual fractions of the bitumen (saturates, monoaromatics, diaromatics, polyaromatics, polar aromatic compounds, asphaltenes) were analysed by gel permeation chromatography to determine the molecular weights. In this chromatography, a porous styrene divinylbenzene copolymer with a maximal pore size of 500 nm was used as stationary phase, while tetrahydrofuran was used as mobile phase. For the evaluation of the measurement results, polystyrene of various molecular weight distributions served as calibration standards. As characteristic values, the number average molecular weight M_n was determined for the original bitumen $M_{n,orig}$, the asphaltenes $M_{n,asph}$, the resins $M_{n,res}$, the polyaromatics $M_{n,polyarom}$, the diaromatics $M_{n,diarom}$, the monoaromatics $M_{n,monoarom}$ and the saturates $M_{n,sat}$. Once more to improve clarity, the values of the mono-, di- and polyaromatics were converted to a number average molecular weight of the total aromatics $M_{n,arom}$. Thereby, for every fraction a duplicate determination was carried out and the average variation coefficient of the different fraction assumed a value of 2.1 wt.%.

4. RESULTS

The evaluation of the measured results bases on the method of multiple regression analysis. This method allows the simultaneous description of one dependent variable by several independent variables [12]. In this work, the rheological parameters were considered as the dependent variables which are the softening point, the logarithm of the complex shear modulus log $|G^*|$ and the phase angle δ at different temperatures. The independent variables are the contents of the individual fractions as well as the molecular weight M_n of the fractions and the original bitumen. The sample size was 33 bitumen samples comprising the 11 bitumen samples in the three different states of ageing: the original state without ageing, the RFT-ageing state and the RFT- and PAV-ageing state. For calculating the regression coefficients *a* of the linear regression functions $y_{rheological} = a_0 + a_1 * x_{1,chemical} + a_2 * x_{2,chemical} + \ldots + a_n * x_{n,chemical}$, the softwares IBM SPSS Statistics 22® and The Unscrambler® X were used. Before the analysis, the considered variables were tested on outliers using box plots. The identified outliers were replaced by the average value of the whole variable. By means of this procedure, the outliers could be eliminated without a reduction of the number of cases.

To verify the determined linear combinations, the data set was split in a calibration set and a validation set including 6 sample and thus approximately 20% of the whole data set. In addition, the coefficient of determination R^2 and the Root Mean Square Error (RMSE) were determined serving as measure for the uncertainty of the prediction. Regarding to the RMSE, the results of the linear functions can be specified as $y \pm 2*RMSEP$ [13; 14].

Remembering the aim of the research, a binder design was aspired allowing the description and forecast of the bitumen properties. Furthermore, the binder design should enable the modification of the bitumen for influencing its properties.
Known from literature, the asphaltene content strongly affects the bitumen properties [2; 7]. Regarding this, as a result of this research some strong correlations between the asphaltene content and several rheological parameters were found. However, not all rheological parameter could be sufficient described by the asphaltene content. Moreover, some bitumen show similar rheological properties but very different asphaltene contents. In the scope of this research, the grades 20/30, 30/45, 50/70 and 70/100 were considered whereby the bitumen of one grade exhibit similar rheological properties. Within these grades with similar rheological properties, the asphaltene content varies by up to 6 wt.% and also the asphaltene content overlaps between the different binder grades.
Because of these reasons, besides the asphaltene content other factors must determine the bitumen properties. One of these factors is e.g. the distribution and the solvatation of the asphaltenes depending strongly of the content and the structure of the other SARA fractions. Regarding this it is known, that both the resins and the saturates exhibit an influence of the viscosity of the bitumen whereby a growing resins content leads to an increase and a growing saturates content leads to a decrease of the viscosity [2]. However, the contents of the SARA fractions are not solely sufficient for describing the rheological properties. Radenberg et al. [15] tried to describe different rheological parameter like the softening point or the viscosity by the contents of the four SARA fractions. But thereby, the coefficients of determinations only assumed unsatisfied values by up to 0.67 [15]. So, besides the content of the SARA fractions also the structure of the fractions seems to be important. An opportunity to capture the structure of the fractions is the determination of the size of the molecules. Because of this, within this research the molecular weight of the several SARA fractions were measured by GPC. Thus, the contents [wt.%] and the average molecular weights M_n [g/mol] of the SARA fractions are available for the description of the rheological parameters.

In a first step, a linear regression function was determined on the base of the content c and the molecular weight M_n to describe the softening point $t_{R\&B}$. Figure 2 presents the result of the multiple regression analyses for this parameter showing the comparison between the measured and the calculated values.

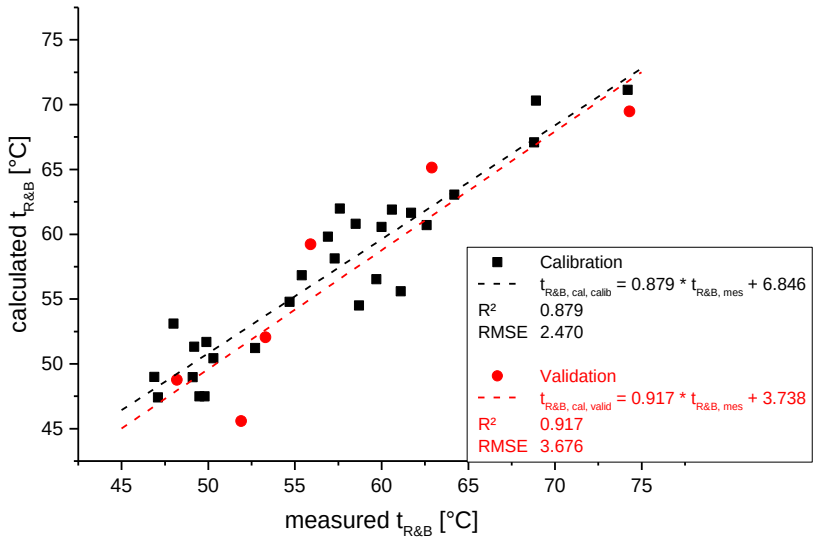

Figure 2 Relationship between the measured and the calculated softening point $t_{R\&B}$ as follow
$t_{R\&B}$ = -1.007 * c_{sat} – 0.477 * c_{arom} + 0.319 * c_{res} + 1.423 * c_{asph} + 0.017 * $M_{n,sat}$ – 0.054 * $M_{n,arom}$ + 0.033 * $M_{n,res}$ – 0.004 * $M_{n,asph}$ + 59.04

Figure 2 shows the high correlation between the measured and the calculated values of the softening point while the legend indicates the parameter of the adjustment. In the figure, the calibration and the validation set are distinguished whereby the black rectangles represents the calibration set and the red points the validation set.
Because of the correlations of determination R^2 with values around 0.90, the adjustment exhibits a very high quality due to both the calibration and the validation. Furthermore, the RMSE assuming values of 2.5 to 3.7°C is in an acceptable range. Due to the quality of this adjustment, the softening point can be described and predicted by the SARA fractions.
According to the effect of the contents of the SARA fractions, the saturates and the aromatics exhibit a negative influence and the resins and asphaltenes a positive influence on the softening point. Because of this, a higher content of

saturates and aromatics results in a decrease and a higher content of resins and asphaltenes in an increase of the softening point and thus the viscosity of the bitumen. These results comply with known knowledge from the literature described above.
In addition to the presented linear combination including four SARA fractions, a further multiple linear regression was carried out considering the contents c and the molecular weights M_n of the six SARA fractions saturates, monoaromatics, diaromatics, polyaromatics, resins and asphaltenes. With coefficient of determination for the calibration set with 0.94 and for the validation set with 0.86, the linear combination also shows a very good description of the softening point. Nevertheless, for the softening point as well as for the further rheological parameters the linear regressions based on the four SARA fractions were used for the binder design because the eight variables allows a high accuracy of the fit without a too high number of independent variables.

Beside the softening point, also the logarithm of the shear modulus log |G*| and the phase angle δ on different temperature levels can be described with the SARA fractions. The results of the multiple linear regression analyses are shown in Figure 3, Figure 4 as well as Table 2 and Table 3.
Concerning the complex shear modulus log |G*|, a growing coefficient of determination with increasing temperature could be determined. From temperatures of 30°C the coefficient of calibrations set assumed values about 0.80 so that very high qualities are achieved. In contrast, the coefficient of the validation set assumed values about 0.80 at every temperature level whereby higher values for the RMSE can be recognized. Because of the coefficient of the calibration, from temperatures of 30°C the logarithm of the shear modulus log |G*| can be described and predicted by the content and the molecular weights M_n of the four SARA fractions.

Due to the regression coefficient, the viscosity-decreasing effect of the saturates and the aromatics as well as the viscosity-increasing effect of the resins and asphaltenes could be found corresponding to the knowledge known from literature and to the results concerning the softening point.
At this point, also a temperature dependence of the adjustment can be recognized. At low temperatures, the influence of the SARA fraction on the rheological bitumen properties seems to decrease. Therefore, at the low temperatures additional or other chemical properties must become more important.

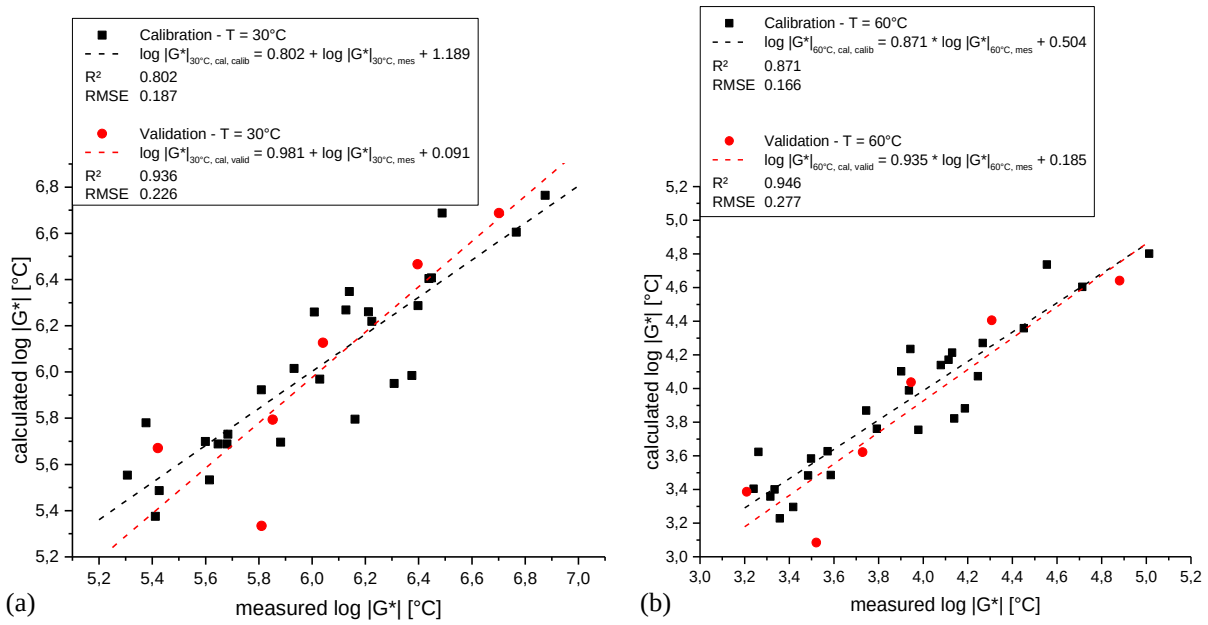

Figure 3 Relationship between the measured and the calculated log |G*| at (a) 30°C and (b) 60°C as follow Table 2

Table 2 Parameter of the linear combinations based on the four SARA fractions for describing the logarithm of the complex shear modulus |G*| on different temperature levels (number of cases: 27 samples for calibration, 6 samples for validation)

	log |G*| at									
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
c_{sat}	-0.035	-0.060	-0.066	-0.061	-0.074	-0.070	-0.081	-0.078	-0.078	-0.074
c_{arom}	-0.025	-0.038	-0.043	-0.046	-0.052	-0.048	-0.049	-0.045	-0.043	-0.038
c_{res}	0.019	0.020	0.024	0.030	0.022	0.022	0.015	0.012	0.010	0.007
c_{asph}	0.003	0.021	0.044	0.065	0.075	0.081	0.081	0.078	0.075	0.068
$M_{n, sat}$	-0.0002	0.0002	0.0004	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$M_{n, arom}$	-0.001	-0.002	-0.002	-0.003	-0.004	-0.003	-0.003	-0.003	-0.003	-0.003
$M_{n, res}$	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
$M_{n, asph}$	-0.0001	-0.0002	-0.0002	-0.0003	-0.0002	-0.0003	-0.0002	-0.0002	-0.0002	-0.0002
Const.	8.687	8.603	7.633	6.504	6.264	5.402	5.170	4.537	4.103	3.589
Calibration										
Slope	0.485	0.647	0.741	0.802	0.837	0.855	0.871	0.875	0.882	0.875
Offset	4.114	2.625	1.755	1.189	0.854	0.663	0.504	0.416	0.332	0.293
R^2	0.484	0.647	0.741	0.802	0.837	0.855	0.871	0.875	0.882	0.875
RSME	0.113	0.146	0.169	0.187	0.183	0.180	0.166	0.156	0.143	0.133
Validation										
Slope	0.938	0.981	1.041	0.981	0.972	0.948	0.935	0.911	0.903	0.865
Offset	0.455	0.100	-0.318	0.091	0.113	0.191	0.185	0.219	0.193	0.234
R^2	0.870	0.883	0.914	0.936	0.951	0.948	0.946	0.939	0.932	0.925
RSME	0.116	0.178	0.207	0.226	0.213	0.229	0.227	0.231	0.229	0.219

In Figure 4 and Table 3 the parameter of the linear regression functions of the phase angle δ were presented whereby for the validation set the coefficients of determination assumed solely values about 0.80 but relatively high values for the RMSE. For the coefficient of the calibration set, an increase until a temperature level of 40°C and then a decrease can be determined. Thereby, between the temperature levels of 10°C and 50°C a coefficient about 0.80 can be recognized. The decreasing value of the coefficient of determination at higher temperature can be explained by the approximation of the phase angle to 90° and thus the approximation to an ideal viscous behaviour of the binder. Because of this approximation, the values become continuously constant so that the quality of the adjustment decreases. At lower temperatures, the influence of the SARA fraction seems to reduce similar to the shear modulus |G*|.
But in the medium temperature range, the description and forecast of the phase angle δ by the contents and the molecular weights of the SARA fractions is possible.
Furthermore, the regression coefficients were considered to evaluate the effect of the fraction contents on the deformation behaviour expressed by the phase angle. Thereby, the sign of the coefficients varies depending on the temperature. In the medium temperature range achieving high qualities of the adjustments the contents coefficients of saturates and aromatics show positive and the resins and asphaltenes negative signs. Therefore, growing contents of resins and asphaltenes lead to a decreasing phase angle and thus to an increasing elastic deformation behaviour of the bitumen which is also known from literature [2].

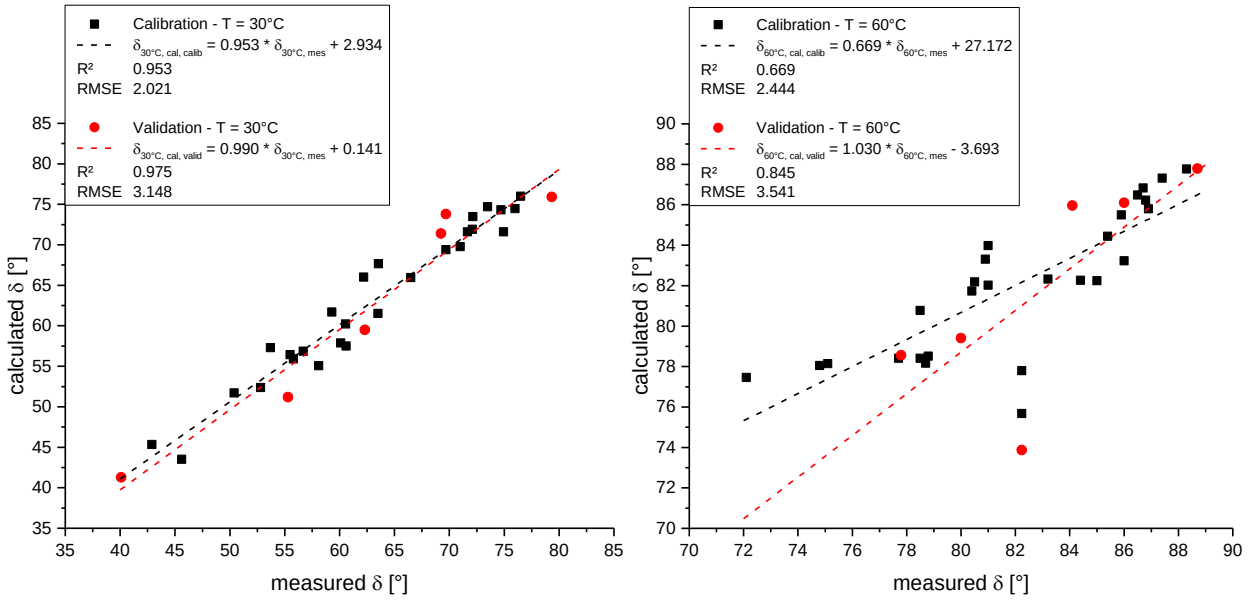

Figure 4 Relationship between the measured and the calculated phase angle δ at (a) 30°C and (b) 60°C as follow Table 3

Table 3 Parameter of the linear combinations based on the four SARA fractions for describing the logarithm of the phase angle δ on different temperature levels (number of cases: 27 samples for calibration, 6 samples for validation)

	δ at									
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
c_{sat}	-0.138	0.672	0.352	0.146	0.314	0.477	-0.208	-0.029	-0.061	-0.205
c_{arom}	0.198	0.534	0.413	0.282	0.288	0.246	0.312	0.220	0.115	0.058
c_{res}	-0.504	-0.367	-0.390	-0.323	-0.149	-0.091	0.039	-0.001	-0.047	-0.169
c_{asph}	-0.500	-1.558	-2.082	-2.196	-1.941	-1.632	-0.536	-0.386	-0.232	-0.254
$M_{n,\ sat}$	-0.005	-0.019	-0.016	-0.011	-0.010	-0.004	0.010	0.009	0.008	0.002
$M_{n,\ arom}$	0.010	0.032	0.023	0.022	0.026	0.023	-0.013	-0.008	-0.008	0.004
$M_{n,\ res}$	-0.004	-0.039	-0.030	-0.027	-0.024	-0.023	-0.007	-0.007	-0.003	-0.012
$M_{n,\ asph}$	0.0005	0.004	0.003	0.004	0.003	0.002	0.002	0.002	0.001	0.001
Const.	45.487	68.281	92.921	102.350	93.661	88.850	83.755	84.605	87.840	100.684
Calibration										
Slope	0.535	0.863	0.923	0.953	0.960	0.953	0.669	0.644	0.595	0.745
Offset	13.274	5.592	4.019	2.934	2.834	3.600	27.172	30.373	35.415	22.632
R^2	0.535	0.863	0.923	0.953	0.960	0.953	0.669	0.645	0.595	0.745
RSME	2.414	2.853	2.552	2.021	1.670	1.535	2.444	1.836	1.312	0.816
Validation										
Slope	0.580	1.047	1.043	0.990	0.951	1.557	1.030	1.159	1.231	1.335
Offset	10.565	-1.916	-2.903	0.141	3.870	-46.367	-3.693	-14.332	-21.000	-30.967
R^2	0.841	0.942	0.965	0.975	0.972	0.801	0.845	0.861	0.856	0.631
RSME	2.878	3.195	3.648	3.148	2.947	6.689	3.541	2.433	1.660	2.081

In a further step, the influence of the different independent variables were deeper investigated. The increasing or decreasing effect of the several variables can be derived from the sign of its regression coefficients and are already described above. Beside the increasing or decreasing effect, the absolute impact of the variables on the rheological parameter can be evaluated. Thereby, the regression coefficients do not directly allow this evaluation because these coefficients depend on the unit of the associated variables. Instead, the regression coefficients have to be standardised. The standardised coefficients are called as *beta coefficients* and give direct information about the influence on the rheological parameter.
The beta coefficients of the contents and molecular weights of the SARA fractions for describing the logarithm of the shear modulus |G*| and the phase angle δ are presented in Table 4. To improve comparison, the four beta coefficients with the highest values marked in bold.

Table 4 Beta coefficients of the linear combinations for describing the logarithm of the shear modulus |G*| and the phase angle δ

	Beta coefficients of the linear combinations of the log |G*| at									
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
c_{sat}	**-0.497**	**-0.547**	**-0.449**	-0.325	**-0.370**	**-0.334**	**-0.395**	**-0.401**	**-0.422**	**-0.441**
c_{arom}	**-0.572**	**-0.558**	**-0.472**	**-0.400**	**-0.412**	**-0.372**	**-0.384**	**-0.374**	**-0.377**	**-0.370**
c_{res}	0.442	0.292	0.257	0.255	0.172	0.163	0.117	0.100	0.086	0.069
c_{asph}	0.065	0.341	**0.525**	**0.620**	**0.657**	**0.687**	**0.697**	**0.710**	**0.716**	**0.725**
$M_{n,\ sat}$	-0.160	0.138	0.176	0.256	0.298	0.261	0.255	0.220	0.230	0.221
$M_{n,\ arom}$	**-0.810**	**-0.864**	**-0.727**	**-0.795**	**-0.820**	**-0.765**	**-0.782**	**-0.762**	**-0.790**	**-0.780**
$M_{n,\ res}$	**0.519**	**0.433**	0.375	**0.363**	0.338	0.322	0.316	0.324	0.320	0.311
$M_{n,\ asph}$	-0.274	-0.270	-0.243	-0.239	-0.204	-0.215	-0.203	-0.204	-0.188	-0.174
	Beta coefficients of the linear combinations of the δ at									
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
c_{sat}	-0.088	0.197	0.086	0.035	0.085	**0.152**	-0.111	-0.021	-0.067	-0.286
c_{arom}	**0.202**	0.252	0.162	0.109	0.126	0.126	**0.266**	**0.259**	0.202	0.129
c_{res}	**-0.509**	-0.171	-0.151	-0.123	-0.064	-0.046	0.033	-0.001	-0.082	**-0.374**
c_{asph}	**-0.564**	**-0.809**	**-0.901**	**-0.937**	**-0.931**	**-0.923**	**-0.504**	**-0.501**	**-0.449**	**-0.629**
$M_{n,\ sat}$	-0.201	**-0.371**	**-0.265**	**-0.183**	**-0.175**	-0.081	**0.359**	**0.436**	**0.572**	0.188
$M_{n,\ arom}$	**0.309**	**0.438**	**0.261**	**0.248**	**0.325**	**0.345**	**-0.332**	**-0.275**	**-0.412**	0.282
$M_{n,\ res}$	-0.067	**-0.316**	**-0.205**	**-0.178**	**-0.178**	**-0.199**	-0.106	-0.137	-0.081	**-0.469**
$M_{n,\ asph}$	0.055	0.185	0.151	0.152	0.127	0.131	0.206	0.230	**0.281**	**0.335**

Based on this table, it can be recognized that the beta coefficients of the different linear combinations are in the same magnitude. So, all variables are necessary for the description of the rheological parameters.
However, depending on the considered rheological parameter and the considered temperature level different variables shows the highest values. For the shear modulus |G*|, the content of the saturates, the aromatics and the content of the asphaltene at higher temperatures as well as the molecular weight of the aromatics seems to be very important. In contrast, for the phase angle δ, the effect of the content of the asphaltenes and especially of the molecular weights of the maltene fractions seems to increase.
But in addition, it should be noted that if a larger number of cases is considered, the beta coefficients and thus the influences of the variables could possibly change.

To sum up the presented results, the findings of this research not only confirm different relationships between the chemistry and the rheology. Moreover, linear regression functions could be determined to describe different rheological parameters by the contents and the molecular weights M_n of the saturates, aromatics, resins and asphaltenes.

In addition analyses, relationships between the chemical composition and structure on the one hand and the sensitivity of ageing on the other hand were tried to find. Therefore, the sensitivity of ageing was quantified by calculated ageing indices (AI) representing the ratio between rheological parameters after long term ageing and rheological parameters in the state without ageing (following [2]). For these analyses, the sample size included just 11 samples because the ageing

indices could only be calculated for the original bitumen. This small number of cases does not allow a division of the data set in calibration and validation set. Due to this small number of cases and the absent division of the data, the found relationships are more trends than resilient functions.
Once again, the softening point, the logarithm of the shear modulus |G*| and the phase angle δ were considered whereby the adjustment for the softening point is shown in Figure 5 and the parameters of the adjustments of the complex shear modulus |G*| and the phase angle δ are presented in Table 5.

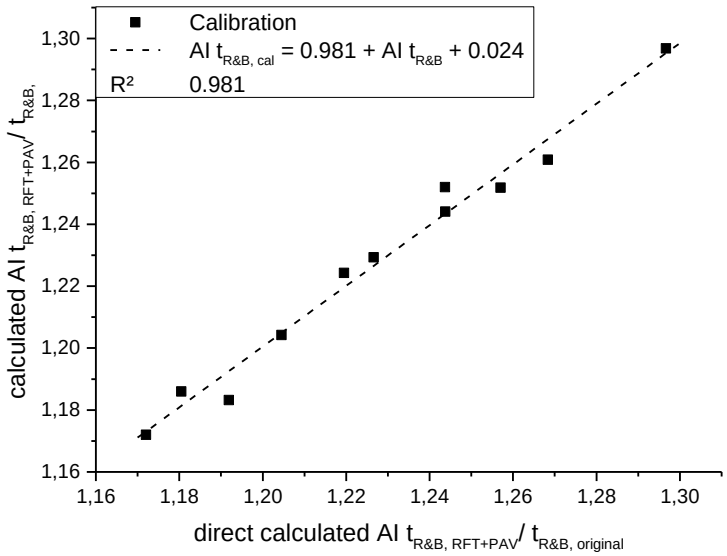

Figure 5 Relationship between the direct from the rheological parameter calculated AI $t_{R\&B,RFT+PAV}$/ $t_{R\&B,original}$ and the calculated AI as follow

$AI\ t_{R\&B} = 0.017 * c_{sat} - 0.014 * c_{arom} + 0.004 * c_{res} + 0.016 * c_{asph} - 0.00003 * M_{n,sat} + 0.00004 * M_{n,arom} + 0.001 * M_{n,res} - 0.00007 * M_{n,asph} - 0,18$

Table 5 Parameter of the linear combinations based on the four SARA fractions for describing the ageing indices of the logarithm of the complex shear modulus |G*| and the phase angle δ on different temperature levels (number of cases: 11 samples for calibration)

	AI log |G*| at				AI δ at			
	20°C	40°C	60°C	80°C	20°C	40°C	60°C	80°C
c_{sat}	-0.002	-0.010	-0.007	-0.006	-0.024	-0.012	-0.015	-0.013
c_{arom}	-0.002	-0.006	-0.005	-0.004	-0.006	-0.005	-0.004	-0.002
c_{res}	-0.002	-0.008	-0.006	-0.004	-0.014	-0.005	-0.008	-0.006
c_{asph}	-0.002	-0.008	-0.004	0.003	-0.013	-0.016	-0.018	-0.012
$M_{n, sat}$	$3.3 \cdot 10^{-5}$	$-1.7 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$	0.0001	$-8.5 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	$6.6 \cdot 10^{-5}$
$M_{n, arom}$	$-1.9 \cdot 10^{-5}$	0.0002	0.0003	0.0001	0.0001	-0.0002	$-5.8 \cdot 10^{-5}$	$-1.4 \cdot 10^{-5}$
$M_{n, res}$	$-3.2 \cdot 10^{-5}$	-0.0004	-0.0003	-0.0004	-0.001	-0.0005	-0.0005	-0.0003
$M_{n, asph}$	$2.2 \cdot 10^{-6}$	$3.6 \cdot 10^{-5}$	$3.3 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$	$7.4 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$3.7 \cdot 10^{-5}$
Const.	1.272	1.905	1.712	1.621	2.217	1.916	1.990	1.631
Calibration								
Slope	0.953	0.610	0.689	0.863	0.793	0.967	0.992	0.972
Offset	0.050	0.450	0.379	0.175	0.157	0.027	0.007	0.026
R^2	0.953	0.607	0.688	0.862	0.794	0.967	0.992	0.972

As can be seen in Figure 5 and Table 5, the coefficients of determination assumed mainly high values indicating of good or very good adjustments. Due to this results, the contents and molecular weights M_n of the SARA fractions in the unaged state allows an estimation of the ageing behaviour of the rheological parameters. For the phase angle, the temperature dependence of the adjustment can be again recognized.

In principle, the chosen approach due to the ageing behaviour seems to be useful. Nevertheless, the analyses should be repeated with a larger number of cases to get more resilient linear combination. So in these results, some not explainable facts appear. Due to the regression coefficients, the results of the analyses seem to be less significant, e.g. the regression coefficients of the fraction contents for describing the ageing behaviour of the phase angle are all negative.

5. THE OPPORTUNITY OF BINDER DESIGN

The discovered relations can be of benefit for the determination and selection of a binder for road construction. Thereby, the benefit is especially important for the forecast of the ageing behaviour of the bitumen which is possible due to the dependencies between the ageing indices and the content and molecular weights of the SARA fractions. On the basis of these relations, predictions about bitumen stability against ageing can be made knowing the change of bitumen parameters after ageing.
Furthermore, the discovered dependencies can be of significance for the recycling of bitumen. During the ageing the binder becomes harder by the inserting distillation-based and oxidation-based ageing. This hardening is the result of shifts of SARA fractions and molecular weights. For recycling, the bitumen properties should be enhanced or restored wherefore additives, so called rejuvenators, are being already added to the demounted bitumen. On the basis of the discovered relations, the shift in the SARA fraction can be comprehended and the amounts and molecular weights, which are required to achieve the original properties of the binder, can be determined. However, the addition of the bitumen's own fractions will not be possible because the large-scale extraction of the SARA fraction is difficult to implement. For alternative additives the content and the molecular weights are not the only important items because the individual SARA fractions are compatible with each other. Possibly, additives showing a differing composition as the bitumen own fractions are not compatible with the other bitumen components and could lead to different influences on the bitumen properties than the bitumen own SARA fractions do. In this respect, a more detailed characterisation of the SARA fraction will be necessary to get more information about the composition of the fractions.

In an imaginary experiment, the vision of an individual binder design can be pursued. On the basis of the discovered relationships, the bitumen can be composed in that way that it shows any desired rheological properties. Therefore, in addition to the discovered relations between the contents and molecular weights of the SARA fractions further relationships must be done looking for including e.g. the ductility and the adhesion behaviour. In consideration of all founded relationships, the optimisation of the required bitumen composition would be possible with the result that the *synthetic bitumen* could be created. Because of the enormous expense of the large-scale separation of the bitumen and of the provision of the individual SARA fractions, this concept will be a vision forever.

6. SUMMARY

The objective of this work was to bring rheological and chemical properties of the bitumen together. As rheological investigation methods, the determination of the softening point (Ring and Ball method) as well as the determination of the complex shear modulus |G*| and the phase angle δ with the Dynamic Shear Rheometer were carried out. As chemical analyses, the separation of asphaltenes to determine the asphaltene content, the further separation of the maltene phase using column chromatography following Šebor at el. [11] to determine the content of the saturates, aromatics and resins as well as the gel permeation chromatography to determine the molecular weight were carried out. The relationships between the rheological and chemical parameters were investigated by multiple regression analyses.
It shows inter alia that the viscosity and the stiffness of the bitumen are dependent on both the contents and the molecular weight M_n of the several SARA fractions.
Furthermore, the contents and molecular weights of the fractions provide information about the sensitivity of ageing and the bitumen behaviour after ageing. The findings can be of benefit for the selection of an appropriate binder for road construction and for the recycling of bitumen.

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REFERENCES

[1] http://www.beton.org/wissen/infrastruktur/bundesfernstrasse/ [downloaded on 08.06.2015]
[2] The Shell Bitumen Handbook; R.N. Hunter, A. Self, J. Read; Thomas Telford Publishing London, 2015
[3] The structure of asphaltenes in bitumen; P.G. Redelius; Road Materials and Pavement Design. EATA 2006, p.143-162, 2006

[4] The colloid structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification; D. Lesueur; Advances in Colloid and Interface Science, (145): p.42-82, 2009
[5] Chemical structure of tar-sand bitumen by ^{13}C and ^{1}H n.m.r. spectroscopic methods; T. Suzuki, M. Itoh, Y. Takegami, Y. Watanabe; Fuel, Vol. 61, p.402-410, 1982
[6] Effects of the asphaltene and resins contents of the bitumens on the water-bitumen interface properties; A. Jada, M. Salou; Journal of Petroleum Science and Engineering 33, p. 185-193, 2002
[7] Bitumen und seine Anwendung; H.J. Neumann; Expert Verlag Grafenau, 1981
[8] 100 Jahre Erweichungspunkt Ring und Kugel – Was kommt danach?; R. Guericke; Straße und Autobahn 7.2010, p. 481-491, 2010
[9] Die Ergebnisse der Bitumen- und Asphaltforschung des Strategic Highway Research Program SHRP – Teil 1: Bitumen-Spezifikationen; P. Bellin; Bitumen 2/95, p. 50-65, 1995
[10] Untersuchung und Bewertung von bitumenhaltigen Bindemitteln für Asphalt mittels Dynamischem Scher-Rheometer (doctoral thesis); T. Hagner; TU Braunschweig, 2003
[11] Optimization of the preparative separation of petroleum maltenes by liquid adsorption chromatography; G. Šebor, J. Blažek, M.F. Nemer; Journal of Chromatography A, 847, p. 323-330, 1999
[12] Multivariate Analysemethoden; K. Backhaus, B. Erichson, W. Plinke, R. Weiber; Springer-Verlag Berlin Heidelberg, 2011
[13] Multivariate Datenanalyse; W. Kessler; Wiley-VCH Verlag Weinheim 2007
[14] The Unscrambler User Manual; CAMO Software AS; 2006
[15] Einfluss der chemischen, rheologischen und physikalischen Grundeigenschaften von Straßenbaubitumen auf das Adhäsionsverhalten unterschiedlicher Gesteinskörnungen; M. Radenberg, M. Gehrke, N. Nytus; AiF-Schlussbericht, 2014

ANNOTATION

This report is based on parts of the research project carried out at the request of the Federal Ministry of Transport and Digital Infrastructure, represented by the Federal Highway Research Institute, under research project No. 7.0249/2011/BRB.
The author is solely responsible for the content.