Binder performance and testing

Post carbon road - The endless cycle of bitumen reuse

Kim Schwettmann[1], Dietmar Stephan[1], Nina Nytus[2], Martin Radenberg[2], Sandra Weigel [3]

[1]Technische Universität Berlin, Group of Building Materials and Construction Chemistry, [2]Ruhr-Universität Bochum, Field of Road Construction, [3]Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Abstract

In Germany, the reuse of asphalt has a long tradition. Since the 1980s, the reclaimed asphalt has been recycled achieving a reuse rate of around 90% and thus a very high value in the last years. In the future, instead of the amount, the quality of the reclaimed asphalt will be more important because the recycled asphalt will be reused again and again. Thus, these asphalt mixes are in the second or even third cycle of reuse. Concerning this situation, the question arises if asphalt can be reused several times without any loss in quality. An important factor affecting the asphalt quality is the binder bitumen. During the production, construction and service life, the ageing of this binder occurs causing a hardening of the bitumen. To compensate this hardening, additives for the reclaimed asphalt in terms of rejuvenation agents (rejuvenators) gain in importance. With these rejuvenators, the physical properties of bitumen can be modified e.g. the hardness and the stiffness reduced. However, the mechanism of the rejuvenation agents and the effects of the bitumen chemistry are largely unknown because the composition of the products varies very strongly. But with growing knowledge about these mechanisms and effects of the rejuvenation agents, the chemical composition and thus the physical and ageing behavior of bitumen can be targeted modified by the use of suitable rejuvenators. In this work, the actual results of the project Postcarbone road should be presented including investigations about the chemical and physical mechanisms as well as the efficiency of different rejuvenators. Further, a model for the cyclic reuse of bitumen should be developed. Based on this model, the choice of a suitable rejuvenation agent for the considered bitumen or rather asphalt should be possible. The project Postcarbone road (392670763) is funded by the German Research Foundation (DFG).

This paper was first published in 2020 in version 1.0 of the proceedings of the 7th E&E Congress. This second edition (version 1.1.) of the proceedings is published in June 2021. The content of this paper has not changed, but the author(s) may have provided additional information in the form of an annex.

1. Introduction

When considering asphalt recycling a widespread method is to add fresh bitumen to the reclaimed asphalt binder which helps to compensate the hardening during ageing and to restore the required paving grade [1]. It can be ascertained that this procedure is about to reach its limits when the life cycles replicate, and the amount of fresh bitumen must be so high that the maximally permitted binder content is exceeded. Nevertheless, to reach the striven bitumen properties, rejuvenators have gained growing importance. So far it is known that rejuvenators can change the physical properties such as a decreasing of the viscosity which can be measured by a declining hardness or rather a reduction of the stiffness [2, 3]. However, the effect on the chemical properties is still poorly understood, particularly the long-term interaction between rejuvenators and bitumen. Therefore, the investigation of the physical and chemical properties is an intermediate target for studying an endless cycle of bitumen reuse.
For characterisation of the binder bitumen, it is possible to subdivide the chemical compounds into four groups, which are called the SARA-fractions (saturates, aromatics, resins, asphaltenes) [4]. Throughout the entire life-cycle process starting by paving and finishing by removing, due to the continuous stresses caused by traffic and weather conditions, a shift of the SARA-fractions occurs [5]. During ageing, the asphaltene content increases whereas the aromatic content decreases, which causes a physically determinable hardening of the material [6].
Past research projects have already investigated the advantages and disadvantages of bitumen and asphalt recycling [7-11]. On the one hand, reusing materials is associated with an improvement of sustainability, and on the other, it comes along with several environmental benefits, like a reduction of aggregates and bitumen [7]. Further, a reduction of bitumen mitigates the overall CO_2-emission because both the extraction and treatment of crude oil to obtain bitumen can be reduced [8]. Another environmental benefit is the reduction of waste material and consequently, the need for less landfill space [7]. Additionally, Zaumanis et al. have highlighted another advantage of reusing asphalt which lies in the opportunity of reducing the pavement construction costs by up to 50-70% [8, 9]. However, there are some disadvantages which must be considered when reusing bitumen and asphalt. As previously mentioned, the material hardens during the life-cycle process and the ageing of bitumen can be determined due to a change in the viscosity. This hardening causes that the material indeed becomes less sensitive to higher temperatures, but the low-temperature behaviour is adversely affected [2,7]. It has been shown that there is a higher risk of low-temperature cracking and fatigue damage [8]. Therefore, with rejuvenators the aim to achieve is to improve low-temperature behaviour [2]. Simultaneously, when using rejuvenation agents, the dosage must be carefully determined in order to prevent an over softening of the binder [9]. This means while improving the low-temperature behaviour, it must be ensured that the high-temperature behaviour is not negatively affected. Furthermore, it was found that the ageing effect on rejuvenated bitumen is more damaging than on virgin bitumen because even if the properties of the aged bitumen can be adequately restored, the rejuvenated bitumen has a higher tendency for ageing [2, 3]. Nevertheless, the promising results of the mentioned research projects are offering a great potential, that the possible disadvantages are accepted, and more research is conducted, for example with the project introduced in the present paper.

2. Experimental programme

The experimental programme of this research project is presented in **Fig. 1**. The experimental programme can be divided into five work packages (WP 0 – WP IV). The main goal of this project is to investigate an endless cycle of bitumen reuse, and to identify the potential limits of multiple reusability.
At the beginning of this research, suitable materials had been selected (WP 0). All chosen materials used in this project are presented in chapter **3. Materials**. While searching for suitable materials, another important step is to develop an ageing method for simulating long-term ageing (WP I). The explanation for considering this specific step is described in chapter **4.1 Ageing procedures**. The third step of the program is the fundamental characterisation of the materials (WP II), which is currently being performed. First results are presented in chapter **5. Results**.
The central part of this project begins with WP III.1 and WP III.2. Hereby, the first challenge is to determine the optimal dosage of the applied rejuvenator. Recent studies have shown that there are no generally valid rules for the application of the optimal amount of a rejuvenator [10]. It has been seen that the amount depends on the rejuvenator and the bitumen type [11]. The differences between WP III.1 and WP III.2 are the bitumen samples. In WP III.1 three different virgin bitumen samples, grade 50/70, are used for simulating multiple cycles of reuse. In WP III.2, the bitumen samples are naturally aged reclaimed bitumen. Based on all the explained preparatory work and the detailed investigations using various test methods (**4. Methods**) the last step WP IV can be carried out pursuing the goal of developing a sustainable model for cyclic rejuvenation. Due to the large number of test results gained by different test methods supporting the analysation and valuation of this, data multivariate evaluation methods are used.

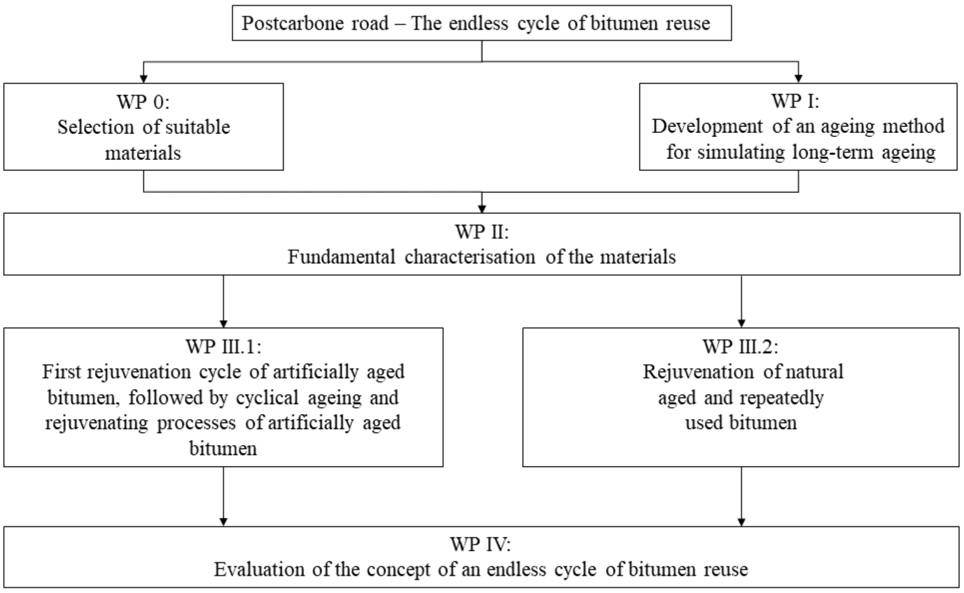

Figure 1: Flowchart of the experimental programme

3. Materials

In this project, the used materials can be divided into three different groups. The first group consists of three bitumen samples from three different refineries named B.1, B.2 and B.3. All three of them belong to grade 50/70, according to EN 12591 [12].
Another group is formed by reclaimed asphalt samples, removed from six different construction sites, using the abstraction method according to DIN EN 12697-3 [13].
The selected reclaimed asphalts (RAP) are:

- RAP-A.1 (municipal road, approx. 15 years)
- RAP-A.2 (municipal road, approx. 9 years)
- RAP-A.3 (federal motorway, binder-layer, approx. 18 years)
- RAP-A.4 (federal motorway, surface-layer, approx. 18 years)
- RAP-A.5 (runway, airport, approx. 20 years)
- RAP-A.6 (highway, binder- and surface-layer, approx. 30 years)

The third category of materials is the group containing the rejuvenating agents. In total there are eight rejuvenators from different companies available for studying the rejuvenating effects on aged bitumen named R.1 to R.8. The differences between the rejuvenators are that they are derived from different sources. While the rejuvenators R.1, R.3, R.4, R.5 and R.8 are declared coming from sustainable raw materials, the rejuvenators R.2, R.6 and R.7 are mineral oil-based products. Especially R.6 (500/650) and R.7 (V6000) are very soft road bitumen and produced according to EN 12591 [12].

4. Methods

4.1. Ageing procedures

The ageing process of bitumen can be divided into two main parts, the short-term and the long-term ageing. Short-term ageing describes the ageing procedure during mixing, spreading and compaction and is mostly simulated with the Rolling Thin Film Oven Test (RTFOT) according to EN 12607-1 [14, 15]. Long-term ageing instead refers to the ageing process during the pavement's service life and the corresponding standard procedure for the simulation is the Pressure Ageing Vessel test (PAV) according to EN 14769 [16]. While the chemical and rheological changes during the short-term ageing are simulated quite realistic, investigations have shown that for long-term ageing simulation, the PAV test is rather unsuitable [14, 17]. During the PAV test, a 3.2 mm thick film of bitumen is exposed to 100 °C and air pressure of 2.07 MPa for 20 h. However, several studies have shown that when it comes to studying the ageing of bitumen ultraviolet radiation should be included [17].
As a result, the first goal is to develop a more precise method for simulating long-term ageing (**Fig. 1**, WP I). Therefore, an oven was designed and built containing ultraviolet radiation. The main wavelength of the UV lamp is 365 nm, and the average intensity on the bitumen surface is about 1 W/cm². Other studies have shown that the effect of UV radiation is recognisable on the low-temperature behaviour [18, 19]. In these cases, the bitumen samples were exposed to UV radiation from 1 h to 16 d. A significant difference between the ovens used in previous studies and

the oven in this project is the average intensity on the samples. In the other projects, the UV lamps had much lower average intensities of 0.3 and 0.6 W/cm² [18, 19].

4.2. Conventional and rheological tests

The classical bitumen tests needle penetration, softening point ring and ball, Fraass breaking point, ductility as well as the rheological bitumen tests using the bending beam rheometer (BBR) and the dynamic shear rheometer (DSR) were realised following the relevant European (EN)-standards.
To describe the rheological properties, comprehensive Temperature-Sweeps (T-Sweep) from -10 to 150 °C in 10 °C-steps were realised. At low temperatures from 30 to - 10 °C, the parallel plate geometry with a diameter of 8 mm (PP08) and a gap of 2 mm has been used. For this temperature range frequencies of 0.1, 1.0, 1.59, 5.0 and 10 Hz have been selected to compare these results with those of the new test methods. At intermediate and high temperatures from 30 to 150 °C, the 25 mm diameter parallel plate geometry (PP25) with a gap of 1 mm and 1.59 Hz were applied.
In addition to these investigations, two further tests with the DSR in a low-temperature range were conducted:

- The Shear-Relaxation-Test (SRV) – A Creep Stress Test at -10 °C that uses the 8 mm diameter parallel plates (rotation, Strain-controlled, 0.1 % deformation).
- The 4-mm DSR (PP04-test) – An oscillation test, performing a frequency sweep from 0.01 to 10 Hz at various temperatures from -20 to 30 °C, using the 4 mm diameter parallel plates.

In addition to the conventional and rheological test methods, the focus of this project is to investigate the chemical compositions.

4.3. FTIR spectroscopy

The FTIR spectroscopy is performed with the device PerkinElmer Spectrum Two FT-IR C 96108. For the investigation of the samples, the attenuated total reflection (ATR) measurement with multiple reflections (zinc selenide crystal, length approx. 50 mm, sample area approx. 575 mm², 25 reflections) is been used. For the measurements, the samples are dissolved in cyclohexane using a mass ratio of 1:3. To provide representative FTIR spectra, the measurements of the samples are carried out within 24 h using an Eppendorf pipette to apply 0,1 ml of the bitumen-cyclohexane-solution on the crystal. After 15 min. the solvent is evaporated, and a thin bitumen film remains. The measurements are carried out with the following settings: 32 scans, a wave number range from 4000 to 600 cm^{-1} and a resolution of 4 cm^{-1}.

4.4. Asphaltene content

The determination of the content of the asphaltenes is carried out with the extraction process as specified by the DIN 51595 [20]. Within this method a bitumen sample of approximately 1.3 g is boiled under reflux in 90 ml of n-heptane for one hour, filtrated with a cellulose filter type 604 ½ (particle retention of 25 µm) and then the filter is washed in a Soxhlet extractor. This first step of the extraction is run with n-heptane to separate the remaining maltenes from the asphaltenes. In a second step, the solvent toluene (70 ml) is to regain the asphaltenes from the filter. Afterwards, the asphaltene-toluene-mixture is evaporated using a rotary evaporator. The remaining asphaltenes are weighed, and the content is determined by the relation to the initial weight of the sample.

4.5. Column chromatography for separation of the maltenes

The residue of the asphaltene separation, the maltenes, is further separated using the column chromatography based on Šebor et al. [21]. This method is used to determine the content of the different bitumen fractions. Therefore, the lower half of the column, which has an inside diameter of 30 mm, is packed with 44 g aluminium oxide Al_2O_3-90 (Merck no. 1.01077) and for the upper half, 33 g silica gel SiO_2 (Merck no. 107734) is used. For providing an even application of the maltenes into the column, they are dissolved in n-heptane applied with a graduated pipette. The solvents which are used afterwards for the separation of the different fractions are given in **Table 1**. Subsequently, the solvents are evaporated using a rotary evaporator and, equally to the asphaltene separation, the results are referred to the weight of the initial sample.

Table 1. Solvents for column chromatography

Fraction	Solvent
Saturates	n-heptane
Monoaromatics	n-heptane / toluene 19:1
Diaromatics	n-heptane / toluene 17:3
Polyaromatics	Toluene
Resins	Toluene/ diethyl ether/ methanol 1:1:3

For further investigation of the components of bitumen gel permeation chromatography (GPC) will be used for obtaining information about the sizes of the molecules of the samples.
Other additional test methods are imaging techniques. As seen in recent studies, to investigate bitumen samples with imaging techniques can provide quite interesting results when analysing the microstructure of bitumen [6, 22]. In this project, the samples are going to be investigated by scanning electron microscopy (SEM) and by laser scanning microscopy (LSM).

5. Results

5.1. Conventional and rheological properties

The conventional binder properties needle penetration and softening point from the three bitumen 50/70 unaged and aged with RTFOT and RTFOT+PAV and the six RAP-binder are shown in **Fig. 2**. As it can be seen with combined ageing of RTFOT and PAV the bitumen 50/70 reached an aging grade which is higher or comparable to two RAP-binders RAP-A.1 and RAP-A.4. The ageing grades of the other four RAP-binders are higher than the aged bitumen 50/70.

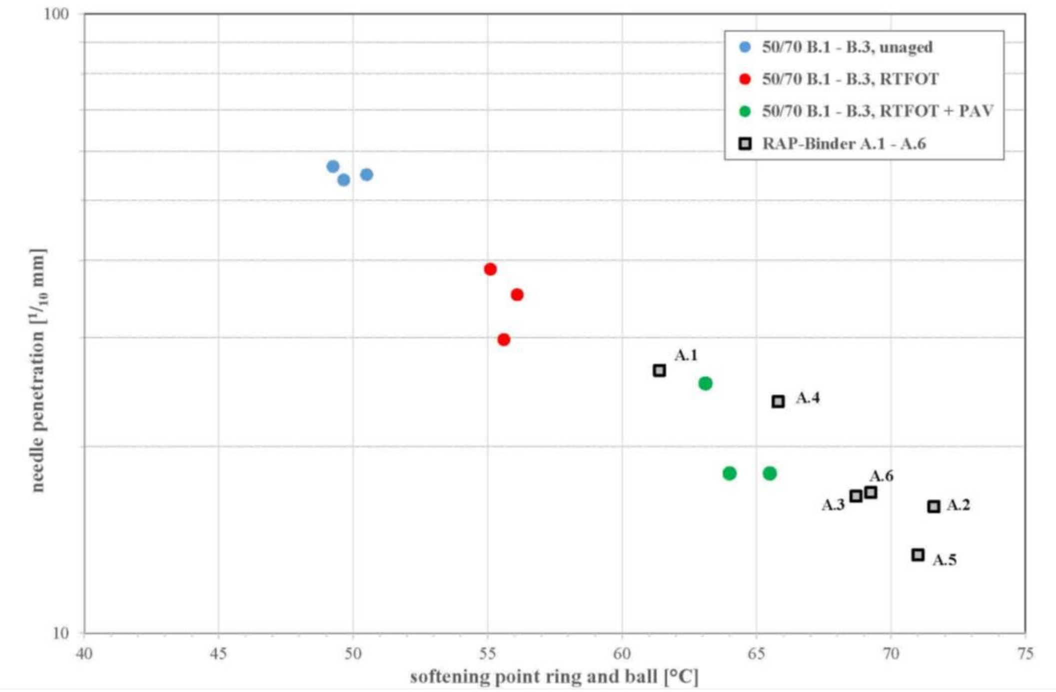

Figure 2: Softening point ring and ball and needle penetration (50/70 unaged and aged and RAP-binder)

The rheological properties of the samples are represented in **Fig. 3** and **Table 2**. **Fig. 3** shows a black-diagram of the three unaged bitumen 50/70 and the six RAP-binders, measured with a frequency of 1,59 Hz. Additionally, delineated is the product R.6 (Penetration 500/650), a very soft road bitumen. Furthermore, the low-temperature-performance of the samples were measured using three different test methods, and the results are shown in **Table 2**. As a characteristic value for the appraisal of the Shear-Relaxation-Test (SRV) the parameter REL_{SRV} is the quotient of the shear stress at the beginning (τ_1) and the end (τ_{30}) of the relaxations phase [23]:

$$\frac{\tau_{30}}{\tau_1} = REL_{SRV} \tag{1}$$

In the 4-mm DSR-test (PP04) the low-temperature-performance was assessed by the phase angle at -20 °C (0.01 Hz). The binders RAP-A.1 and RAP-A.2 have the poorest low-temperature-performance in all three test methods. It can also be seen that the sample RAP-A.5, which is declared as a 20-year-old airport runway still, shows good low-temperature characteristics compared to the other reclaimed asphalt samples. Whereas RAP-A.2 has the poorest low-temperature-performance in all the test methods although it is the sample with the shortest service life.

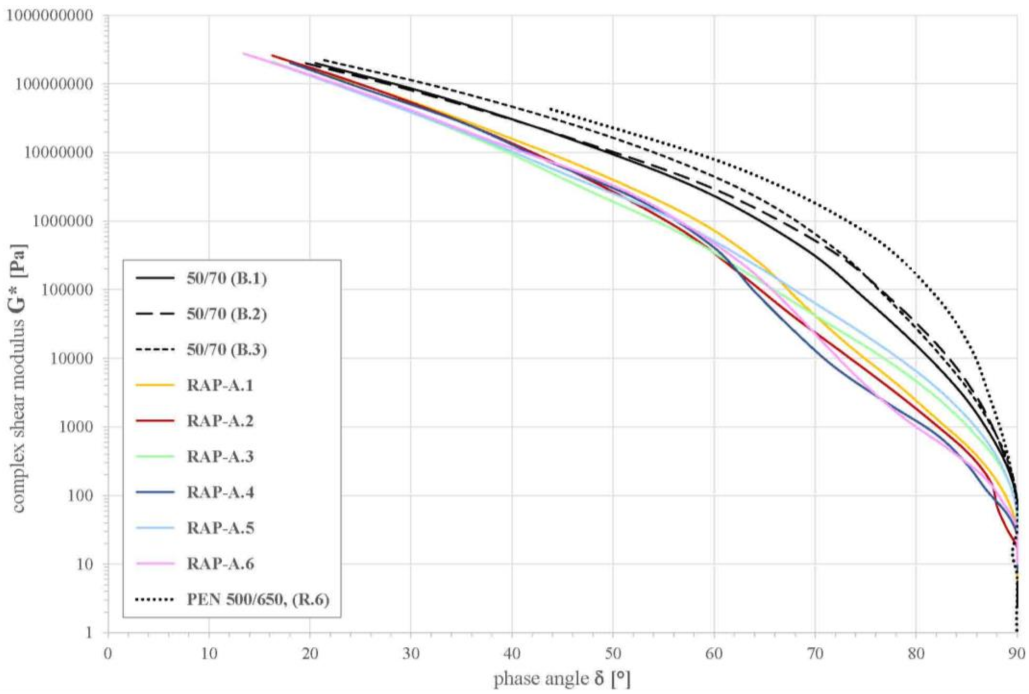

Figure 3: Black diagram; Temperature-Sweep with DSR, frequency 1.59 Hz

Table 2. Low-temperature-performance, BBR, DSR (SRV) and DSR (PP04)

Sample	BBR			DSR (SRV)	DSR (PP04)
	T(S=300) [°C]	T(m=0.3) [°C]	Delta TC	REL_{SRV} [%]	Phase angle δ at -20°C, f=0.01 HZ [°]
B.1 - unaged	-19.0	-21.0	1.0	0.6	20.6
B.1 - RTFOT + PAV	-15.6	-15.6	0.0	3.3	16.7
B.2 - unaged	-17.2	-19.2	2.0	0.9	18.9
B.2 - RTFOT + PAV	-14.3	-14.6	0.3	3.7	14.4
B.3 - unaged	-17.2	-19.6	2.4	0.4	20.6
B.3 - RTFOT + PAV	-14	-15.2	1.2	2.4	17.2
RAP-A.1	-13.5	-10.3	-3.2	4.6	14.5
RAP-A.2	-14	-12.3	-3.2	5.1	13.8
RAP-A.3	-16.3	-12.6	-3.7	3.3	17.0
RAP-A.4	-15.7	-14.5	-1.2	2.9	16.7
RAP-A.5	-20.4	-21.8	1.4	1.3	20.3
RAP-A.6	-17.2	-17.7	0.5	3.1	17.1

5.2. FTIR analysis

FTIR spectra of B.1, B.2 and B.3 are shown in **Fig. 4**. For analysing and presentation of the measured data, the reflectance spectra were converted in absorbance spectra. A typical FTIR spectrum of bitumen shows peaks in wave number ranges from 3500 to 2500 cm^{-1} and from 1800 to 690 cm^{-1}. The important peaks of the spectra are labelled, showing the aliphatic hydrocarbons, the aromatics, the carbonyls and the sulfoxides [24, 25].
In this case, by using FTIR spectroscopy, it enables the identification of the functional groups responsible for ageing characteristics. By comparing the differences between the ages of all three samples, it becomes visible that mostly the carbonyl and the sulfoxide compounds are increasing due to increasing age. Carbonyls and sulfoxides compounds are the indicators for the degree of oxidation, which is known being a typical ageing mechanism of bitumen [17, 26]. To present the increase of the carbonyls and sulfoxides other studies chose a determination of an ageing index, but **Fig. 4** clearly shows the growth of the peaks and consequently further representation methods become dispensable. It is also recognised that in this case the aliphatic hydrocarbons apparently are not identifiable affected by the binder oxidation. However, these results must be treated with some reservation, because for other bitumen samples the results may differ. **Fig. 5** presents the absorption values for the six reclaimed asphalt binders. According to the shown test results, RAP-A.1 (blue), RAP-A.3 (pink) and RAP-A.4 (yellow) could be samples with a higher ageing grade due to their higher degree of oxidation indicated by the carbonyls and sulfoxides. In comparison to the known

information about the reclaimed asphalt binders the samples RAP-A.1, RAP-A.3 and RAP-A.4 are not the samples with the highest service life.

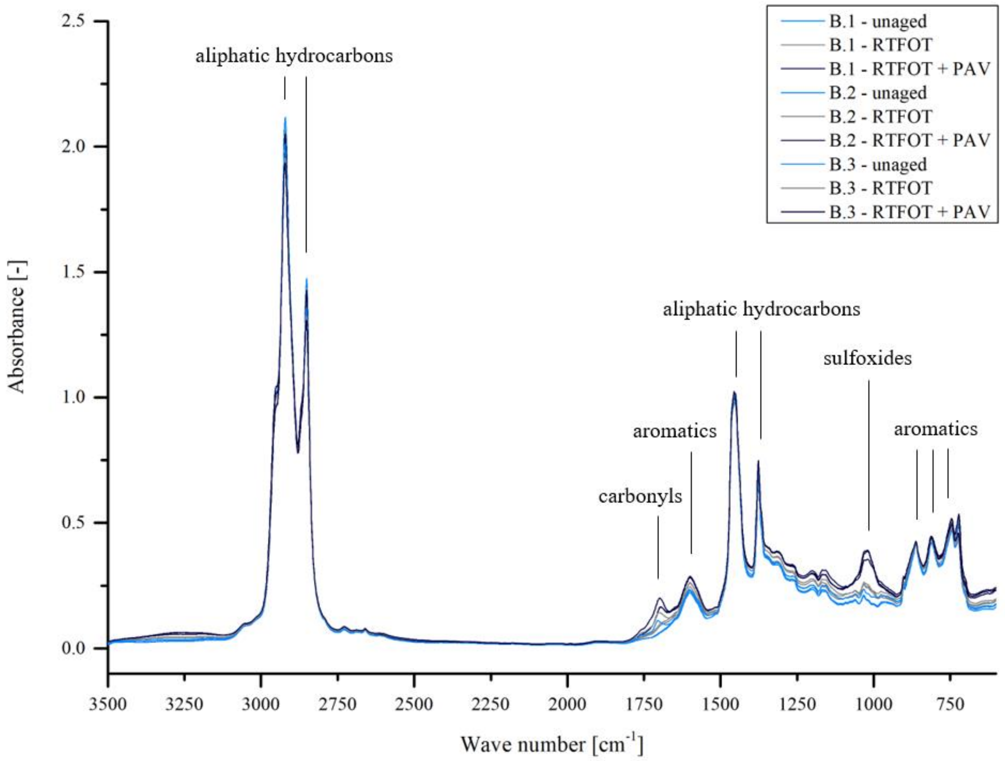

Figure 4: FTIR spectra of bitumen samples B.1, B.2 and B.3, unaged (blue), RTFOT (grey) and RTFOT+PAV (black)

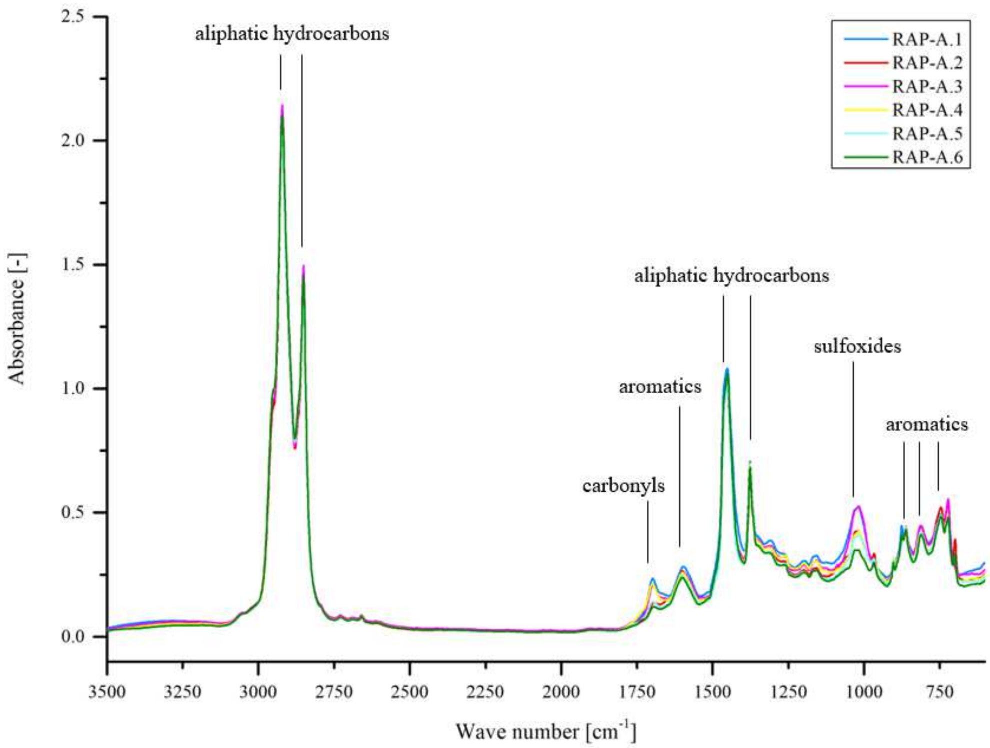

Figure 5: FTIR spectra of reclaimed bitumen samples RAP-A.1 - RAP-A.6

The rejuvenators were also investigated using FTIR spectroscopy following the same defined preparation terms and measurement settings as for the bitumen samples (**Fig. 6**). The aim of this investigation was to gain more knowledge about the composition of the rejuvenators. The spectra of rejuvenator R.6 (dark blue) and R.7 (orange) equals a spectrum of a typical bitumen sample. These results may confirm that rejuvenator R.6 and R.7 are bitumen and are derived from crude oil. Further parallels are discovered between the rejuvenators R.1 (light blue), R.3 (blue) and R.4 (pink). These three rejuvenators are declared to originate from sustainable raw materials, and due to the results, it can be presumed that the rejuvenators are derived from the same raw material although they are coming from different manufacturers. Furthermore, even though the sample R.5 (green) it is also obtained from bio-renewable resources the FTIR spectrum differs considerably. This observation can also be made for rejuvenator R.2 (red), which is a mineral oil-based product but very different from the other two mineral oil-based products. A similarity between FTIR spectra for all the seven rejuvenators are the peaks at the aliphatic hydrocarbons between 3000 and 2750 cm^{-1}. However, this result clarifies the organic character of the rejuvenators, which can be an essential element for the compatibility of bitumen and rejuvenator.

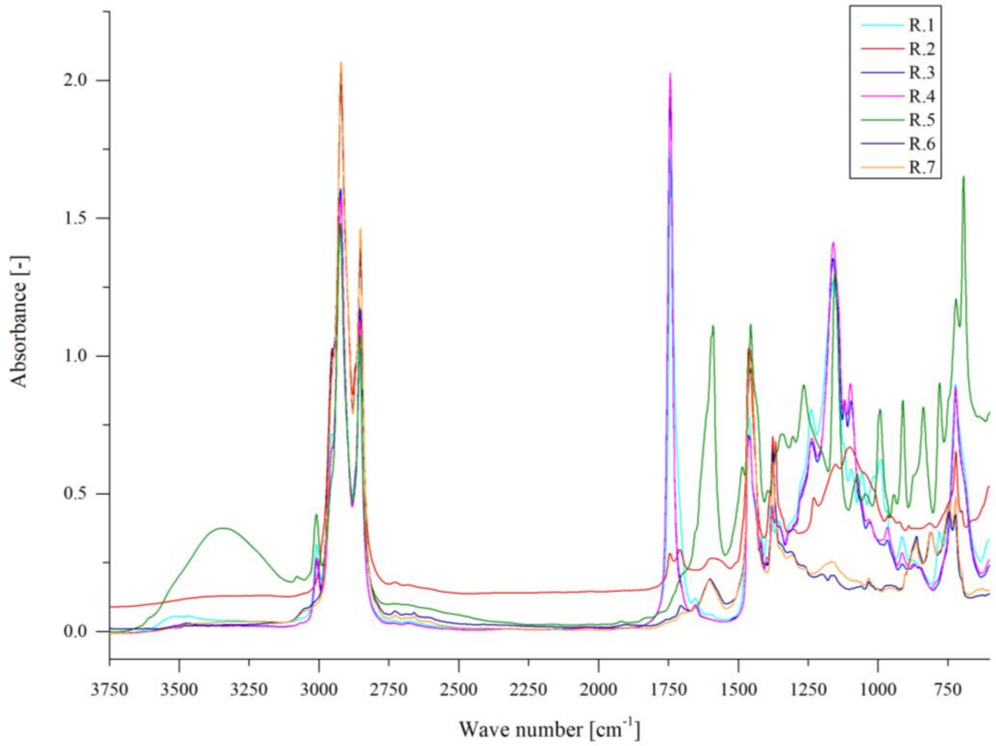

Figure 6: FTIR spectra of the rejuvenators R.1 - R.7

5.3. Asphaltene content and column chromatography

For an extensive determination of the fundamental characteristics, the samples were further investigated by using asphaltene separation and column chromatography. For each sample a parallel double determination has been made. So far, the method was conducted on nine bitumen samples. **Fig. 7** displays the results for the unaged bitumen samples. The results for the six RAP-samples in **Fig. 8** show that the highest asphaltene contents are found in RAP-A.1, RAP-A.3 and RAP-A.4, which match with the FTIR spectra. However, these three samples are not the oldest samples used in this project. The samples with the highest service life are RAP-A.5 and RAP-A.6. It is generally understood, that during ageing the asphaltene content increases whereas the aromatic content decreases [6]. In principle, this statement is correct, when comparing different ages of the same bitumen sample. For the characterisation of different bitumen samples from different refineries, this statement should be treated with caution because even unaged samples with the same grade can show different asphaltene contents (**Fig. 7**).

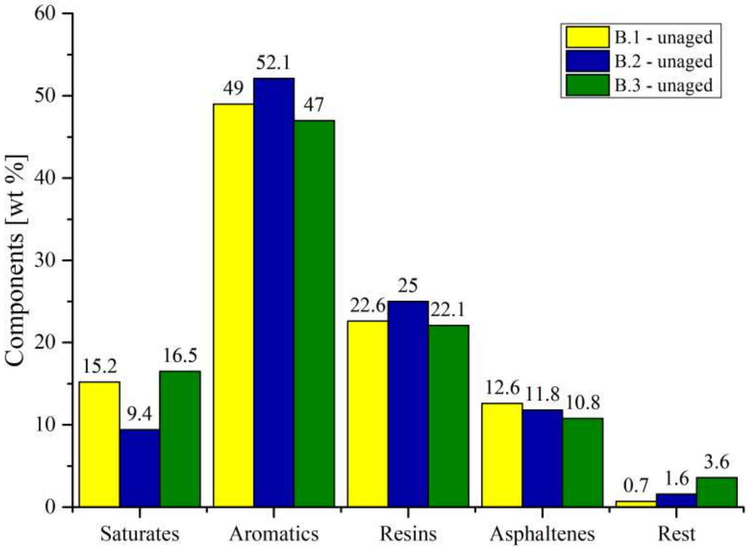

Figure 7: Results of asphaltene content and column chromatography for unaged bitumen samples B.1 (yellow), B.2 (blue) and B.3 (green)

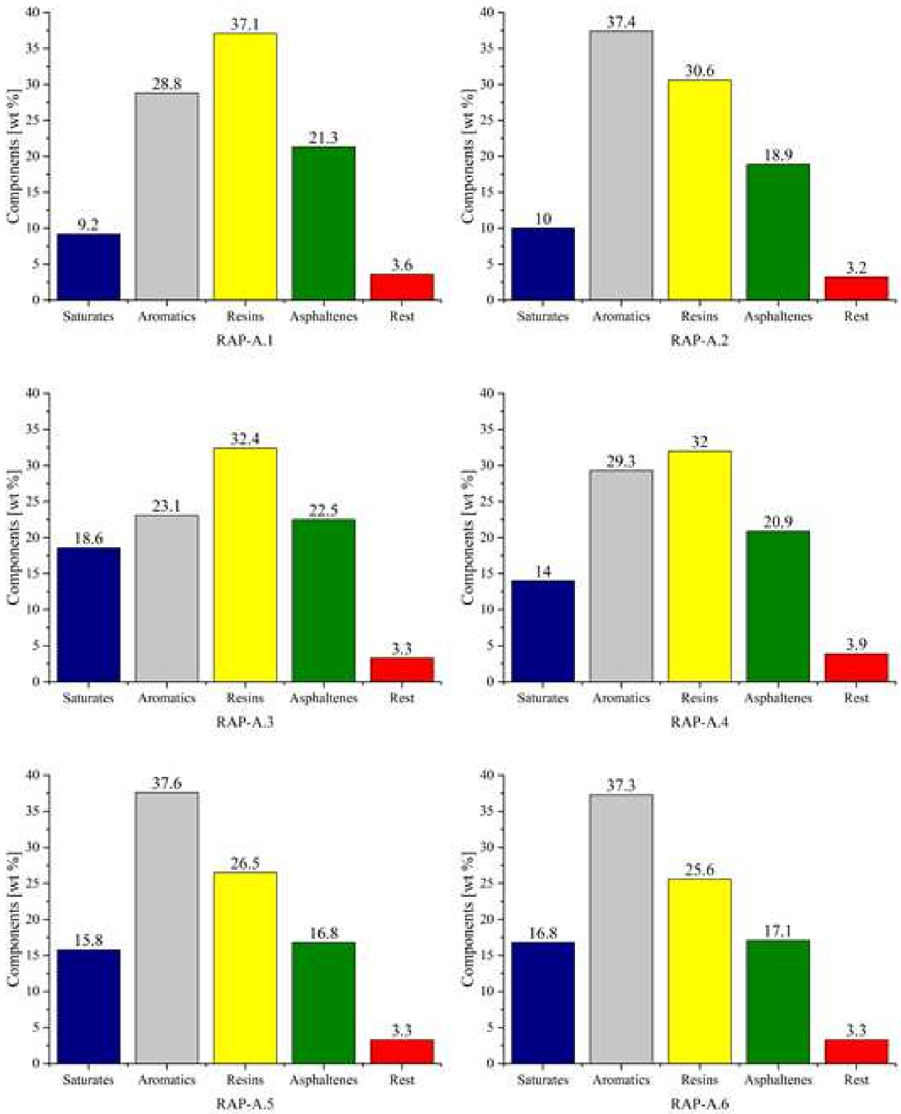

Figure 8: Results of asphaltene content and column chromatography for reclaimed bitumen samples RAP-A.1 - RAP-A.6

6. Conclusion

Initial insights about the fundamental characteristics of the chosen materials are represented in this paper. The results show the importance of an extensive knowledge about the material properties for the pursued development of a sustainable cyclic-rejuvenation-model. First goal of this project is to develop a more precise method for simulating long-term ageing and based on the presented intermediate results, the following conclusions can be drawn:

- In principal, there is a recognisable correlation between the asphaltene content and measured stiffness of bitumen. Considering only one individual bitumen sample, it is true that with an increasing of the ageing rate also the asphaltene content and the stiffness are increasing. However, it is not possible to compare the absolute values of the asphaltene content of different samples and draw conclusions directly to the respective ageing grade. This indicates that the bitumen characteristics are dependent on the entire composition and not just on few parameters such as the asphaltene content. Thus, an overall assessment of all properties becomes essential.
- The comparison of the conventional, rheological and chemical results shows that for the determination of the ageing grade all measurements must be considered. While, with the conventional and rheological test methods, the samples RAP-A.2, RAP-A.3, RAP-A.5 and RAP-A.6 have the highest ageing grade. The chemical investigations instead show a higher ageing grade for the samples RAP-A.1, RAP-A.3 and RAP-A.4.
- For developing method for simulating long-term ageing the results have shown that samples with a shorter service life can still have a high ageing grade. It is confirmed that the ageing grade of a bitumen sample is not directly related to the service life but dependent on many other factors such as void content or the stresses during the service life.

ACKNOWLEDGEMENTS

The project Postcarbone road (392670763) is funded by the German Research Foundation.

REFERENCES

[1] A. Dony, J.Colin, et al., Reclaimed asphalt concretes with high recycling rates: Changes in reclaimed binder properties according to rejuvenating agent, Construction and Building Materials, 41,2013,175-181, http://dx.doi.org/10.1016/j.conbuildmat.2012.11.031

[2] A. Grilli, M.Gnisci, et al., Effect of ageing process of bitumen and rejuvenated Bitumen, Construction and Building Materials, 136,2017, 474-481, https://dx.doi.org/10.1016/j.conbuildmat.2017.01.027

[3] M. Radenberg, Einsatz von Rejuvenatoren bei der Wiederverwendung von Asphalt, Straße und Autobahn, 67, 2016,19-25

[4] R.N. Hunter, A.Self, et al., The Shell Bitumen Handbook, Shell International Petroleum Company Ltd,2015

[5] V. Hirsch, O.Ripke, Lernen von der Straße – Offenporige Asphalte. Straße und Autobahn,1.2008,12-19

[6] D. Großegger, Microstructural aging of bitumen, E&E Congress Prague, 2016, https://dx.doi.org/10.14311/EE.2016.135

[7] T. Moghaddam, H.Baaj, The use of rejuvenating agents in production of recycled hot mix asphalt: A systematic review, Construction and Building Material, 114,2016,805-816, https://dx.doi.org/10.1016/j.conbuildmat.2016.04.015

[8] M. Zaumanis, R.B.Mallick, et al., 100% hot mix asphalt recycling: challenges and benefits, Transportation Research Procedia, 14,2016, 3493-3502, https://dx.doi.org/10.1016/j.trpro.2016.05.315

[9] M. Zaumanis, R.B.Mallick, et al., 100% recycled hot mix asphalt: A review and analysis, Resources, Conservation and Recycling, 92,2014, 230-245, http://dx.doi.org/10.1016/j.resconrec.2014.07.007

[10] M. Zaumanis, R.B.Mallick, et al., Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures, Construction and Building Materials, 71, 2014, 538-550, http://dx.doi.org/10.1016/j.conbuildmat.2014.08.073

[11] T. Blomberg, M.Makowska, et al., Laboratory simulation of bitumen aging and rejuvenation to mimic multiple cycles of reuse, Transportation Research Procedia, 14,2016, 694-703, https://dx.doi.org/10.1016/j.trpro.2016.05.335

[12] EN 12591, Bitumen and bituminous binders-Specifications for paving grade bitumens,2009

[13] EN 12697-3, Bituminous mixtures-Test methods-Part 3: Bitumen recovery: Rotary evaporator,2013

[14] R. Çetinkaya, Bewertung der Einflussgrößen auf die thermisch-oxidative Alterung von Bitumen in Asphalt. Straße und Autobahn, 5,2011,319-325

[15] DIN EN 12607-1, Bitumen and bituminous binders-Determination of the resistance to hardening under the influence of heat and air-Part 1: RTFOT method,2007

[16] EN 14769, Bitumen and bituminous binders-Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV),2012

[17] R. Tauste, F.Moreno-Navarro, et.al., Understanding the bitumen ageing phenomenon: A review, Construction and Building Materials, 192,2018, 593–609, https://doi.org/10.1016/j.conbuildmat.2018.10.169
[18] J. Hu, S.Wu, et al., Effect of ultraviolet radiation in different wavebands on bitumen, Construction and Building Materials, 159,2018, 479-485, https://doi.org/10.1016/j.conbuildmat.2017.10.117
[19] J. Hu, S.Wu, et al., Effect of ultraviolet radiation on bitumen by different ageing procedures, Construction and Building Materials, 163,2018, 73-79, https://doi.org/10.1016/j.conbuildmat.2017.12.014
[20] DIN 51595, Testing of petroleum products-determination of the content of asphaltenes-Precipitation with heptan, 2000
[21] G. Šebor, J.Blažek, et al., Optimization of the preparative separation of petroleum maltenes by liquid adsorption chromatography, Journal of Chromatography A ,847,1999,323-330 , https://doi.org/10.1016/S0021-9673(99)00329-5
[22] H.R. Fischer, E.C,Dillingh, et al., On the microstructure of bituminous binders, Road Materials and Pavement Design, 15,2014,1-15, http://dx.doi.org/10.1080/14680629.2013.837838
[23] M. Gehrke, Komplexe Charakterisierung bitumenhaltiger Bindemittel anhand temperatur,- frequenz,- und belastungsabhängiger Kennwerte, Bochumer Universitätsverlag,2017
[24] J. Lamontagne, P.Dumas, et al., Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens. Fuel, 80, 2001,483-488, https://doi.org/10.1016/S0016-2361(00)00121-6
[25] V. Mouillet, F.Farcas, et al., Ageing by UV radiation of an elastomer modified bitumen, Fuel, 87,2008,2408-2419, http://dx.doi.org/10.1016/j.fuel.2008.02.008
[26] J.C. Petersen, R.Glaser, Asphalt oxidation mechanisms and the role of oxidation products on age hardening revisited, Road Materials and Pavement Design, 12 ,2011,795-819, https://doi.org/10.1080/14680629.2011.9713895

Annex

Since 8/2018, when the 1st version of the paper was submitted, the research project “Post carbon road – The endless cycle of bitumen reuse” has been successfully continued. At the present state the project has entered WP III.1. By the end of the project, a total of four ageing and rejuvenation cycles will be carried out. In order to start the cyclical reuse, the fundamental characterisation of the materials was completed, a more suitable method to simulate in-situ ageing was developed and the determination of the optimal dosages of rejuvenators was investigated. In this annex, a brief overview of the results and achievements until the first ageing and rejuvenation cycle is given.

1. AGEING PROCEDURE

The objective from WP I was to select a method to simulate the long-term ageing of bitumen more realistically. To achieve this goal, the common ageing methods RTFOT and PAV were investigated, as well as ageing procedures with UV radiation. This process included tests with pure UV radiation, along with a combination of common methods and radiation, as well as the common methods exclusively. A total of three different light sources were used, each with different radiation intensities in the range of 1,000 W/m² to 10,555 W/m². The results of these test series showed that the influence of an exposure to UV radiation is probably limited to the uppermost zone of the top layer, as changes after UV radiation were only measured at very low layer thicknesses. Even with a combination of the common methods and radiation, the influence of UV radiation was hardly measurable. The most precise approximation of the rheological bitumen properties could be achieved with a combination of RTFOT and double PAV (RTFOT + 2xPAV). Thus, this combination was determined as the ageing method for the further course of the project, although there was still a difference in the FTIR spectra of artificial and in-situ aged bitumen.

2. DETERMINATION OF THE DOSAGES OF THE REJUVENATORS

In oder to start with the first rejuvenation cycle, the method to determine the dosages of the rejuvenators had to be specified. Therefore, the eight rejuvenators (R.1-R.8) were mixed with one of the three long-term aged road bitumen 50/70 at three different dosage levels, producing 24 variants in total. For the evaluation of the chosen dosages, the equiviscous temperature $EG^*_{15kPa}T$ was used. This temperature is a parameter that shows a high correlation with the softening point ring and ball [1]. A linear relationship was found between the temperature and the dosage. Based on this, the dosage amounts for the first cycle were calculated. Depending on the type of rejuvenator, very different dosages were required to reach the equiviscous temperature of the fresh bitumen. Lower dosages were more sufficient for the plant-based rejuvenators than for the petroleum-based products. The calculated required dosages of the two soft bitumen, R.6 and R.7, ranged from 35 to 47.5 wt.% and were no longer considered in the further course of the project.

3. STATUS QUO – FIRST REJUVENATION AND AGEING CYCLE

The first rejuvenation cycle was carried out with a total of 18 variants, made from three aged bitumen (B.1, B.2,B.3 - RTFOT + 2xPAV) and six rejuvenators (R.1, R.2, R.3, R.4, R.5, R.8). The presented data were determined with temperature-frequency sweeps performed in a temperature range from -20 to +150 °C with different measuring geometries and frequencies for various temperature ranges. In addition, the low temperature behaviour of the rejuvenated bitumen samples was investigated with the BBR.

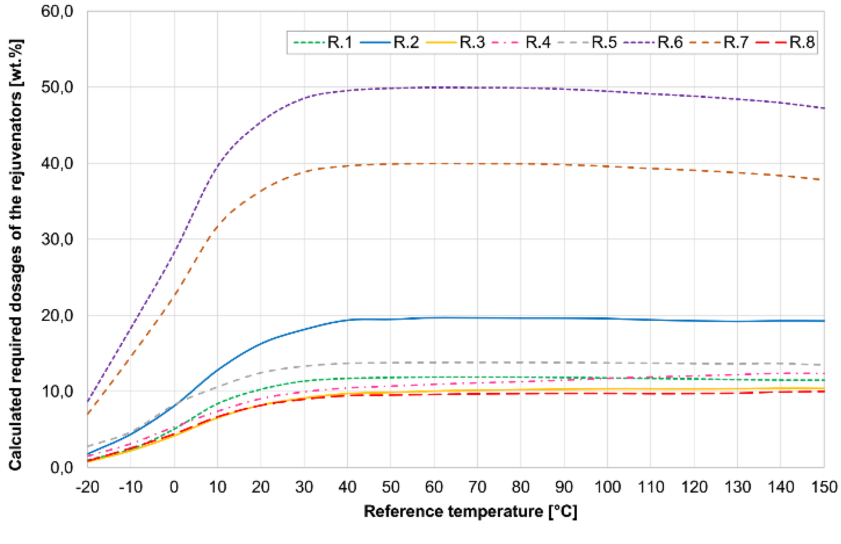

Figure 1: Calculated required dosages of the rejuvenators depending on the complex shear modulus G*at the respective reference temperature

Due to limited space, **Table 1** only displays the results of the bitumen B.1 rejuvenated with all six rejuvenators (B.1 aged + R.1-R.8), representatively for the results of B.2 and B.3. The equiviscous temperature $EG^*_{15kPa}T$ shows that the stiffness of the bitumen can be reduced by all six products. The smallest differences to the unaged initial sample could be achieved with the rejuvenators R.1, R.4, R.5 and R.8. However, the phase angle at $EG^*_{15kPa}T$ indicates that there are significant variations within the rejuvenators' mechanisms. The slightest changes were measured with the rejuvenators R.5 and R.8. The phase angle with the largest deviation appeared with rejuvenator R.2, the only petroleum-derived product. Clear differences between the rejuvenators were also found by the investigation of the cold behaviour of the bitumen-rejuvenator mixtures. In the BBR tests, compared to the unaged road bitumen, the mixtures with the products R.5 and R.8 have a similar cold behaviour. Even lower critical temperatures and significantly better cold behaviour could be found for the products R.1, R.2, R.3 and R.4. The results can be interpreted as a widening of the plasticity range of the rejuvenated bitumen compared to the unaged bitumen 50/70. This creates the potential to reduce the rejuvenator dosage without the risk of early cracking. For a more detailed investigation concerning the influence of the reference temperature on the calculated required dosages, the complex shear modules G* of the preliminary tests (T-sweeps at 1.59 Hz) were used to calculate the required dosages for the entire temperature range (**Fig. 1**). This reveals an almost constant, calculated required dosage for a reference temperature from 40 to 150 °C. Below 40 °C, the calculated required dosage significantly decreases with a reduction of the reference temperature. In summary, the first rejuvenation process displays clear differences between the equiviscous temperature $EG^*_{15kPa}T$ and the tests at low temperatures (BBR, $EG^*_{50MPa}T$). Thus, the equiviscous temperature $EG^*_{15kPa}T$ should be questioned in being the solitary criterion for determining the dosage amount of the rejuvenators. After the rejuvenation process, all 18 samples were aged again (aged = RTFOT+2xPAV) to investigate the ageing behaviour of the rejuvenated samples. Comparing the differences of the equiviscous temperatures $EG^*_{15kPa}T$ and the corresponding phase angles, the variants with rejuvenators R.5 and R.8 exhibited a stronger tendency to age. After ageing, these two variants show a comparable cold behaviour to the road bitumen samples in the unaged state. The cold behaviour of the other four variants improved in comparison to the aged bitumen B.1 before the rejuvenation. The phase angles of all variants decreased due to ageing and, as was found in the first rejuvenation cycle, this effect cannot be reversed by all six rejuvenators. The possibility, that the phase angle might decrease with each further ageing cycle, could indicate the limits of an "endless" cyclic reuse.

Table 1. First cycle of reuse - Results of bitumen sample B.1

Sample	$EG^*_{15kPa}T$ [°C]	Phase angle at $EG^*_{15kPa}T$ [°]	$EG^*_{50MPa}T$ [°C]	Phase angle at $EG^*_{50MPa}T$ [°]	T(S=300MPa) [°C]	T(m=0,3) [°C]	ΔTc [°C]
B.1 - unaged	49.9	79.9	1.3	33.6	-19.0	-21.0	2.0
B.1 - aged	69.9	71.6	8.4	28.4	-14.9	-12.0	-2.9
B.1 aged + R.1	50.9	71.3	-8.0	31.5	-29.0	-29.4	0.4
(B.1 aged+ R.1) aged	69.0	66.4	-2.0	26.7	not determined		
B.1 aged + R.2	59.7	65.9	-6.0	22.7	-29.4	-22.4	-7.0
(B.1 aged + R.2) aged	79.9	58.8	-3.6	20.2	not determined		
B.1 aged + R.3	56.0	69.5	-5.6	30.2	-27.8	-28.0	0.2
(B.1 aged + R.3) aged	76.8	63.1	-0.4	25.1	not determined		
B.1 aged + R.4	50.5	69.0	-12.0	29.6	-31.8	-30.7	-1.1
(B.1 aged + R.4) aged	70.9	63.7	-4.4	25.5	not determined		
B.1 aged + R.5	51.4	76.5	-2.0	31.4	-23.0	-22.9	-0.1
(B.1 aged + R.5) aged	86.1	61.0	2.8	22.0	not determined		
B.1 aged + R.8	53.4	75.1	-0.8	32.5	-23.3	-23.4	0.1
(B.1 aged + R.8) aged	79.7	65.6	4.7	24.8	not determined		

In general, the equiviscous temperatures $EG^*_{50MPa}T$ did not increase as much as the equiviscous temperatures $EG^*_{15kPa}T$ and a significant correlation between the BBR results T(S = 300 MPa) and the equiviscous temperatures $EG^*_{50MPa}T$ could be found. Having gained this comprehensive knowledge of the first rejuvenation and ageing cycle of different bitumen, in further work packages these cycles will be repeated to evaluate the approach of an endless reuse cycle of bitumen. In addition to the artificially aged bitumen, naturally aged reclaimed asphalt samples will also be investigated to verify the results (WP III.2). Finally, in the last work package IV, a calculation model for the determination and evaluation of a cyclic reuse of bitumen shall be developed. In addition to the selection of a suitable rejuvenator, the goal is also to investigate the possibility of a forecast model for required intervention times.

REFERENCES

[1] M. Radenberg, M. Gehrke, Assessing bitumen in the whole service-temperature-range with the dynamic shear rheometer, 6th Eurasphalt & Eurobitume Congress, 2016, dx.doi.org/10.14311/EE.2016.259