

1 **An Alternative Approach towards Aging of Asphalt Binder**

2

3 **Bernhard Hofko**

4 Vienna University of Technology, Institute of Transportation, Research Center of Road
5 Engineering

6 Gusshausstrasse 28/E230-3, 1040 Vienna, Austria

7 Tel: +43-664-6104988; Fax: +43-1-58801-23399; Email: bernhard.hofko@tuwien.ac.at

8

9 **Florian Handle**

10 Vienna University of Technology, Institute of Materials Chemistry

11 Getreidemarkt 9, 1060 Vienna, Austria

12

13 **Lukas Eberhardsteiner, Markus Hospodka, Ronald Blab**

14 Vienna University of Technology, Institute of Transportation, Research Center of Road
15 Engineering

16 Gusshausstrasse 28/E230-3, 1040 Vienna, Austria

17

18 **Josef Füssl**

19 Vienna University of Technology, Institute for Mechanics of Materials and Structures

20 Karlsplatz 13, 1040 Vienna, Austria

21

22 **Hinrich Grothe**

23 Vienna University of Technology, Institute of Materials Chemistry

24 Getreidemarkt 9, 1060 Vienna, Austria

25

26

27 Word count: 4,737 words text + 11 tables/figures x 250 words (each) = 7,487 words

28

29

30

31

32

33

34 Submission Date: October 22nd 2014

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

ABSTRACT

Awareness increases that natural, financial and energy resources are scarce goods. Thus, there is a growing demand not only for high quality but also for efficient infrastructure. Efficiency, in this case, aims for optimization of cost and energy consumption over the complete life cycle of a construction. The objective is to build long lasting infrastructure with low maintenance demands and high recycling potential after having reached the end of its service-life. For bituminous bound materials, aging of asphalt binder has a crucial impact on the durability and recyclability. Since asphalt binder is of organic nature, thermal and oxidative aging by chemical and structural changes occurs when producing and laying asphalt mixes, as well as over its service-life. Increasing stiffness and brittleness of the binder makes the pavement more prone to thermal and fatigue cracking. An interdisciplinary research project works towards a better understanding of the physico-chemical fundamentals of asphalt binder aging, as well as on the impact of binder aging on the mechanical properties of asphalt binder and asphalt mixes. By extensive chemical and mechanical analyses, a new model has been developed to explain aging on the physico-chemical level, as well as on the mechanical level to explain aging comprehensively. Aging can be determined mathematically by micro-mechanical modeling. With the presented model at hand, changes in asphalt binder due to aging (increasing brittleness and stiffness) can be explained.

Keywords: asphalt binder aging, asphalt mix, mechanical modeling, laboratory aging of asphalt mix, chemical analysis

1 INTRODUCTION

3 Motivation

4 Efficiency of road infrastructure today does not only include optimized structural performance in
5 terms of resistance to fatigue, rutting and low-temperature cracking, but also in terms of cost and
6 energy consumption. Long-lasting pavement structures should minimize cost and energy
7 consumption throughout their in-service life. In addition high recyclability is another objective to
8 ensure that high value asphalt mix layers can be re-used after the end of their in-service life by
9 recycling in new pavements. These considerations are reflected by the legal framework, e.g. the
10 European Waste Framework Directive (WFD, 2008/98/EG) (1). It follows a waste management
11 hierarchy: prevent, recycle, recover, and dispose.

12 The asphalt binder has an essential impact on the increasing susceptibility of asphalt mix layers to
13 cracking. Increasing brittleness and stiffness make flexible pavements more prone to
14 low-temperature and fatigue-induced cracking which decreases the life-span significantly. For this
15 reason, aging resistant binders account for higher durability and thus cost and energy efficient
16 pavements. In addition, aging of asphalt binder and the related changes in its characteristics limit
17 the recyclability of asphalt mixes (2, 3) .

19 Objectives

20 Binder aging plays an important role regarding improved cost- and energy efficiency of road
21 pavements. Thus, within the on-going research project "Oekophalt - Physico-chemical
22 fundamentals on asphalt binder aging for efficient recycling of asphalt mixtures" an
23 interdisciplinary team works towards the following objectives:

- 24 • Understanding reasons and processes of asphalt binder aging on physico-chemical and
25 mechanical level (4-11)
- 26 • Impact of asphalt binder aging on the mechanical behavior of asphalt mixes
- 27 • Expanding the assessment of aging resistance of binders
- 28 • Developing improved laboratory aging methods for asphalt mix testing to reflect
29 field-ageing more accurately.

30 This project was designed to bridge the gap between fundamental and applied sciences. A joint
31 taskforce of researchers from applied material science, material chemistry, and mechanical
32 modeling was formed to tackle these questions.

33 The interdisciplinary nature of the co-operating researchers enabled the formulation of a new,
34 holistic understanding of asphalt binder aging, based on the conjuncture of the three fundamentally
35 different perspectives of physico-chemical analysis, micro-mechanical modeling, and mechanical
36 material characterization. Comprehensive analysis of asphalt binder and asphalt mix aging in the
37 field and in the lab has been carried out. Specimen were obtained from a number of test sites on the
38 public road network, which were chosen to reflect a range of aging (between 3 and 24 years) and in
39 different states of performance. Additionally, a test field was constructed in September 2012 to
40 monitor field aging of unmodified and SBS-modified binder and asphalt mixes in close detail (12).
41 This paper focuses on one outcome of the project: a micro-physical and micro-mechanical model
42 of asphalt binder to describe aging and effects of aging on the mechanical behavior of asphalt
43 binder.

44
45
46

POTENTIALS AND SOURCES FOR ASPHALT BINDER AGING

Determining cause and effect for asphalt binder aging has been the starting point for numerous research studies (e.g. (13)). However, the question was included into the presented project to close some gaps and illustrate the physico-chemical fundamentals related to asphalt binder aging. It is important to understand existing potentials and vulnerabilities of asphalt binders regarding aging. As asphalt binder was conclusively shown to be an inhomogeneous material, the micro-structure of the material has to be considered one of those potential factors.

A detailed fractionation of different asphalt binder samples according to their polarity was carried out. The basic for fractionation is ASTM D4124 (14), but in contrary to the standard the samples were separated into more fractions, as shown in FIGURE 1. More than 20 different fractions were analyzed by different spectroscopic and microscopic means. The results were the basis for a revised model of the micro-structure and thus binder aging, which is presented later on in this paper.

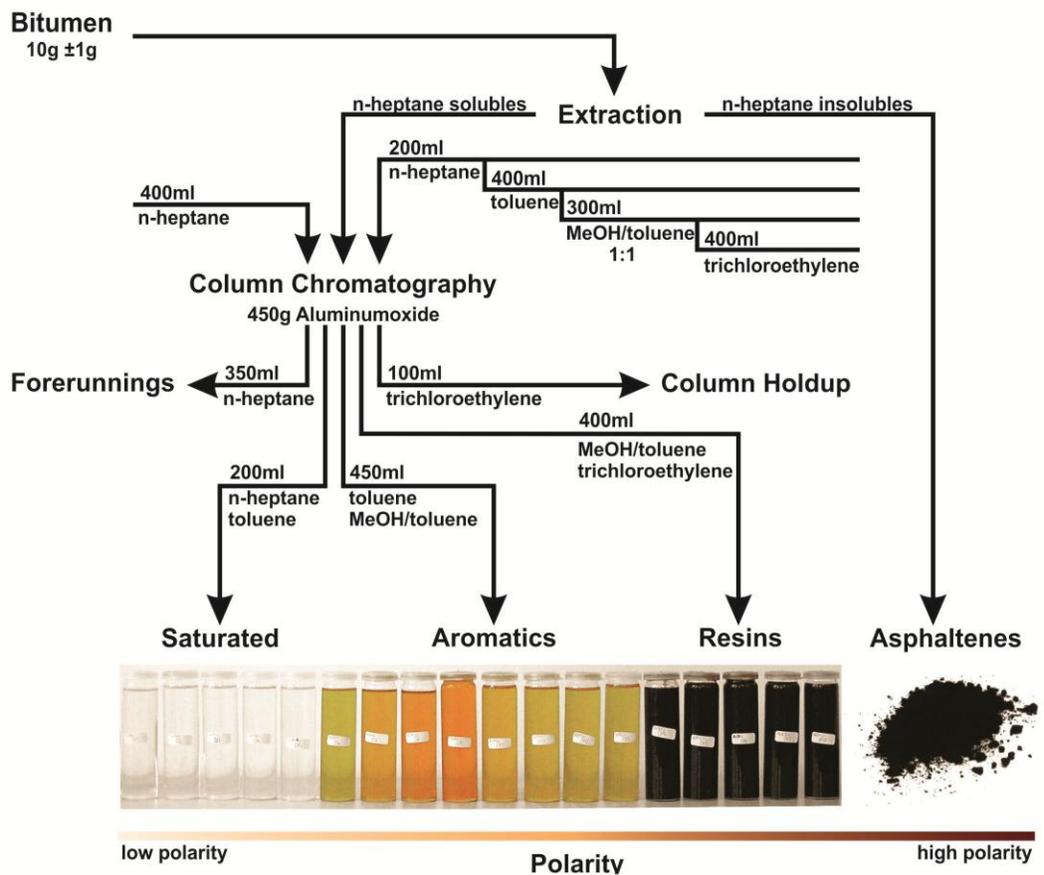
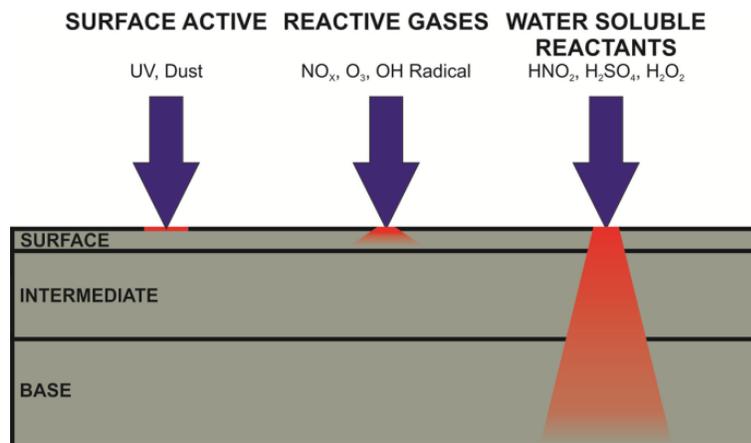


FIGURE 1 Binder fractionation in terms of polarity (15).

Short-term aging (STA) of asphalt binder is well documented and described in literature. STA occurs during mixing and compaction of asphalt pavements and within the next several hours thereafter, while the material is cooling down and expressing its micro-structure. It is possible to distinguish two basic effects of the harsh manufacturing conditions: a) Thermal aging is characterized by thermal decomposition of meta-stable molecules and evaporation of volatile components and b) Oxidative aging by oxidation of susceptible molecules (13). Both are promoted

1 by the elevated temperatures and the high specific surface provided during mixing and laying.
2 Additionally, synergetic effects of both processes have to be considered as molecules fragmented
3 by oxidation may well be prone to evaporation. Long-term aging (LTA), however, occurs while the
4 pavement layer is in-service under climate and traffic loading and is far less understood. Although
5 studies addressing LTA exist, research works are fragmented and much scientific discussion is
6 going on in the community.
7 Considerations on atmospheric chemistry to isolate reactants available in the field serve as a
8 natural starting point, when determining which external factors could have an impact on LTA (16).
9 Studies usually state that atmospheric oxygen and UV radiation are main sources for aging. It has
10 to be noted that aging due to UV does occur but is limited to the upper few micrometers of the
11 binder. Also, atmospheric oxygen is not the only available oxidant and possibly only responsible
12 for a part of field aging. Other reactive gases like nitric oxides and especially ozone are available
13 as well, because exhaust gases promote their formulation. Concentrations of these gases (some
14 ppbs) are clearly below the level of atmospheric oxygen but the oxidation potential is significantly
15 higher than the potential of relatively inactive oxygen - at least at temperatures occurring in the
16 field ($< +65^{\circ}\text{C}/150^{\circ}\text{F}$). The oxidizing gases mentioned above can explain aging in upper layers
17 close to the surface. Water soluble oxidants, like HNO_3 , H_2SO_4 or H_2O_2 can penetrate even deeper
18 into a pavement structure. Again, the concentration may be low but once the substances have
19 penetrated the structure, they may stay there for a considerable time and thus, work promote aging
20 far more severe than their direct impact might infer. An overview of proposed aging sources and
21 their significance for different pavement layers is provided in FIGURE 2.
22
23



24
25

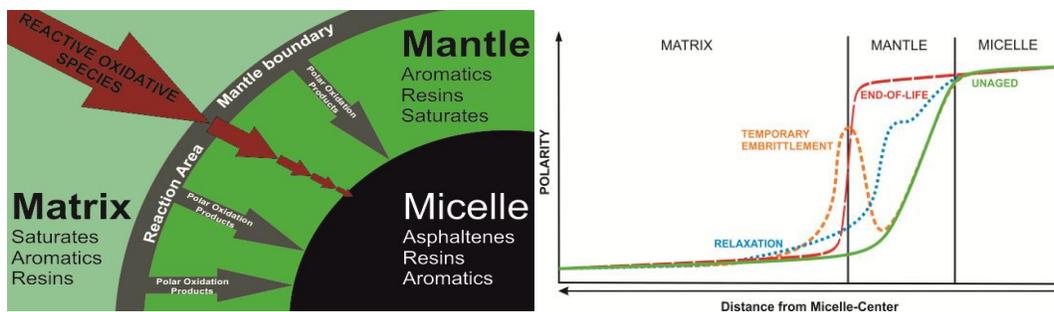
26 **FIGURE 2 Available oxidants for aging of asphalt binder and asphalt mixes (15).**

27 **MICROPHYSICAL MODEL FOR ASPHALT BINDER AGING**

28 Different ideas on the structural composition of asphalt binder exist. A widely accepted idea is the
29 micelle model (17). Basic idea of this model is that asphalt binder is a dispersion of non- or lowly
30 soluble molecules (micelles) within a matrix phase. However, the model is not to be confused with
31 the classical micelle method, which assumes the existence of high weight asphaltenes, which were
32 consecutively proven to be wrong (18). Different studies (19-26) provide arguments for the
33 micelle model and the fractionation analysis gave further evidence that highly polar asphaltenes
34 are dispersed within a lowly polar matrix (maltene phase) of aromatics and saturates. To create a
35 working dispersion, the highly polar asphaltenes have to be surrounded by a shell with a

1 continuous polarity gradient to avoid phase separation processes. This state is shown in the right
 2 diagram in FIGURE 3 as the green line for the unaged asphalt binder. Whereas the lowly polar
 3 maltene phase is inactive in terms of oxidation, the oxidation potential increases with increasing
 4 polarity. Since the highly polar asphaltene core is surrounded by a shell, the reactive oxidant
 5 species (ROS) interact with the shell primarily, leading to the formation of a reaction area rich in
 6 polar constituents (orange line). This effect can be healed by self-association processes leading to
 7 the diffusion of high-polar material into the micelle core, isolating it from the apolar matrix and
 8 leading to the reformation of an intact, if slightly reduced, shell (blue line). With increasing aging,
 9 the process of oxidation leads to the disintegration of the shell, eventually reaching the core after
 10 all. This state is shown in the right diagram in FIGURE 3 as the red dotted line. Due to increasing
 11 oxidation of the shell, its polarity increases as well. This leads to a loss of compatibility between
 12 micelles and matrix due to the rising gap in polarity. This gap in polarity can be seen as a
 13 predetermined breaking point at the interface of shell and matrix. Macroscopic and mechanical
 14 testing correlates these effects to brittleness with progressing aging processes.

15



16
17

18 **FIGURE 3** Reactive oxidant species (ROS) interacting with asphalt binder (left) and microphysical model of
 19 binder aging (right).

20

21 MICROMECHANICAL MODEL OF ASPHALT BINDER AND ITS AGING

22 Based on the physico-chemical analysis of asphalt binder and the microphysical model presented
 23 in the section above, another objective of the research was to establish a micromechanical model
 24 of asphalt binder to analyze the impact of the microstructure on the macroscopic mechanical
 25 behavior of asphalt binder and impacts of aging on microstructure and mechanical behavior.

26 For this, the following steps were taken:

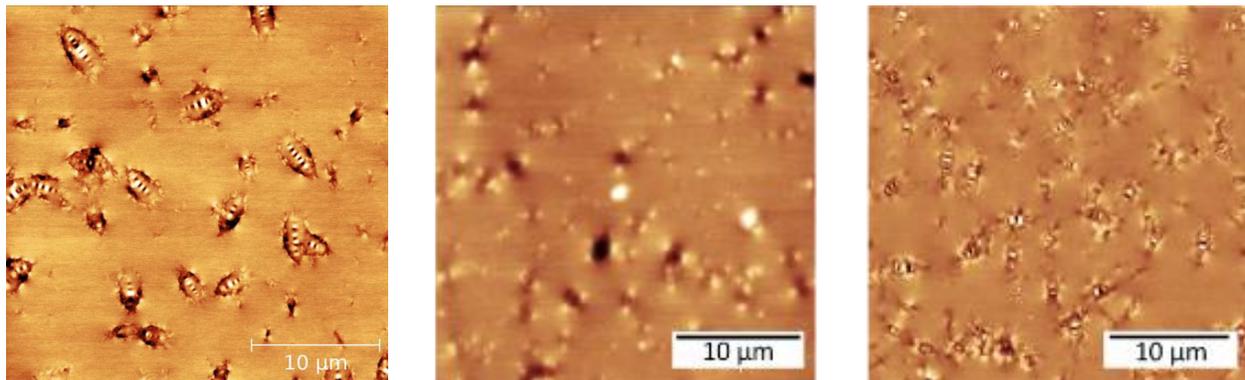
- 27 • An unmodified binder PG 58-22 was fractionated according to ASTM D 4121-01 (14) into
 28 the maltene and asphaltene phase. Precipitated blends of maltenes and asphaltenes with
 29 different well-defined asphaltene concentrations were produced.
- 30 • Atomic force microscopy (AFM) was carried out on the virgin binder, the maltene phase
 31 and the precipitated blend with the same asphaltene concentration as the virgin binder to
 32 verify that the microstructure is re-established after blending of maltenes and asphaltenes.
- 33 • Creep-recovery (CR) tests were carried out at different temperatures on the virgin binder
 34 and the precipitated blends to study the impact of maltene and asphaltene on the overall
 35 mechanical behavior.
- 36 • A micromechanical model was established according to results of physico-chemical and
 37 mechanical analysis of the samples.
- 38 • The same binder was aged using RTFOT and PAV to simulate long-term aging. The aged
 39 samples were again fractionated into the maltene and asphaltene phase, precipitated blends

1 were produced. CR tests were run and analyzed to study the impact of aging on
2 microstructure and mechanical behavior.

3 To study the impact of both major fractions of asphalt binder, the maltene phase and the
4 asphaltenes on the mechanical behavior, an unmodified binder PG 58-22 with an asphaltene
5 concentration of 7.79 vol% according to (14) was separated into the n-heptane soluble maltene
6 phase and the n-heptane non-soluble asphaltene phase based on the procedure proposed by ASTM
7 D 4121-01 (14). After extraction, n-heptane was evaporated from the maltene phase and both,
8 asphaltenes and maltenes were dissolved in toluene and blended to samples with different
9 well-defined asphaltene concentrations in the blend. By evaporating the toluene, asphaltenes were
10 re-dispersed in the maltene phase and thus, precipitated blends were produced.

11 To investigate whether the precipitated blends produce a similar microstructure as the virgin
12 binder, AFM was carried out on the virgin binder, the pure maltene phase and the precipitated
13 blend with comparable asphaltene concentration (7.77 vol.%) (27). Topographical images of all
14 three samples are shown in FIGURE 4. The left image shows the virgin samples. The characteristic
15 “bee” structure or cantana phase is clearly visible. The second picture from the left shows the
16 extracted maltene phase with no asphaltenes present in the sample. No cantana phase can be
17 visualized, whereas on the right image, the bee structure is re-established in the precipitated blend.
18 The AFM images provide strong evidence that the procedure of creating precipitated blends result
19 in a similar microstructure as the virgin binder sample. Since the cantana phase is not visible in the
20 pure maltene phase, this can also be taken as evidence that the inclusions are related with the
21 presence of asphaltenes in the material.

22



23
24

25 **FIGURE 4 AFM images of virgin asphalt binder (left), extracted maltene phase (middle) and precipitated**
26 **blend (right).**

27 Creep-recovery (CR) tests were carried out on a dynamic shear rheometer (DSR) to obtain the
28 material behavior. While a constant torque M is applied for 1800 s on an asphalt binder film
29 (diameter $d = 25$ mm, height $h = 1$ mm), the deflection $\varphi(t)$ is measured. From $\tau = 2M/\pi \cdot r^3$ and
30 $\gamma = r \cdot \varphi(t)/\pi$, the creep compliance

$$31 \quad J_{\text{exp}}(t) = \frac{\gamma(t)}{\tau} \quad (1)$$

32 can be obtained. These tests were run at temperatures in a range from -5°C to $+15^{\circ}\text{C}$. The full
33 experimental program is given in TABLE 1.

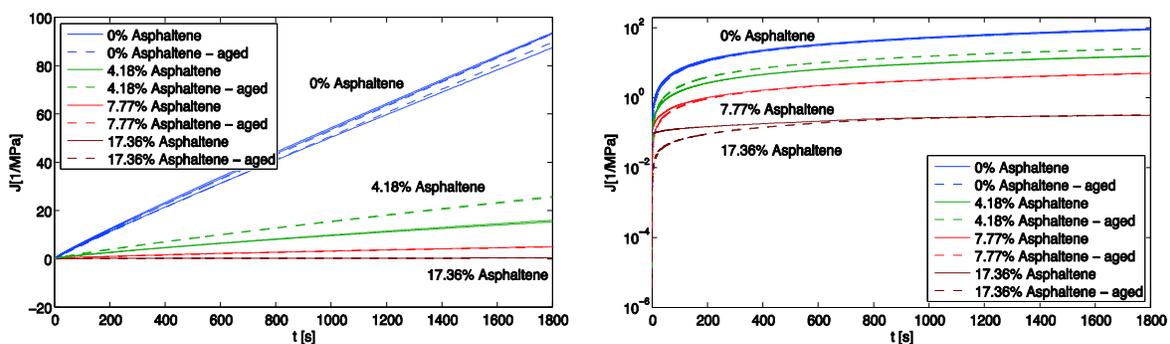
34
35

1 **TABLE 1 Test program for creep-recovery (CR) tests on precipitated blends.**

Asphaltene concentration	Test temperature		
	-5°C	+5°C	+15°C
0 vol.%	●/○	●/○	●/○
4.18 vol.%	●/○	●/○	●/○
7.77 vol.%	○	●/○	○
12.32 vol.%		●	●
17.36 vol.%	○	●/○	○
26.71 vol.%		●	

2 ● ... tests on unaged binder, ○ ... tests on RTFOT+PAV aged binder

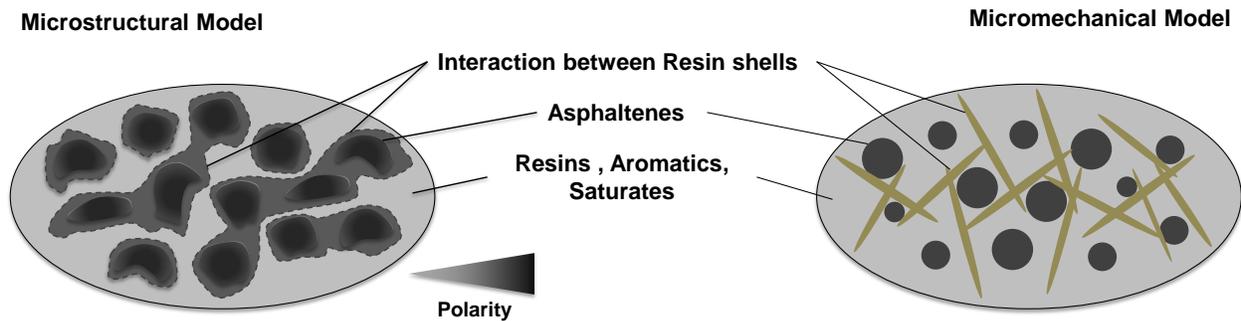
3
 4 FIGURE 5 shows the results of CR tests on unaged and lab-aged precipitated blends with varying
 5 asphaltene concentration at +5°C. Three replicates were run for each material. While increasing
 6 asphaltene concentration causes a decrease in creep compliance and hence stiffer material
 7 behavior, the creep rate dJ/dt decreases with increasing asphaltene concentration until almost
 8 elastic behavior is reached at an asphaltene concentration of 17.36 vol.%. Adding only low
 9 amounts of asphaltenes (4.18 vol.%) to the maltene phase leads to a strong increase in stiffness
 10 (compare blue and green lines in FIGURE 5): The creep compliance at 1800 s is at a mean value of
 11 90 1/MPa for the pure maltene phase and drops to a mean value of 20 1/MPa for the blend with
 12 4.18 vol.% of asphaltenes, which indicates an increase in stiffness by the factor of 4.5. This shows
 13 that by adding asphaltenes, a structure in asphalt binder is introduced that strongly affects the
 14 mechanical behavior, similar to precipitation hardening used in metal hardening. Another key
 15 finding is that aged and unaged samples with the same asphaltene concentration show no
 16 significant differences in their creep curves. This in turn means that the material behavior of
 17 maltenes and asphaltenes are not affected by aging. Thus, the detected increase in the asphaltene
 18 concentration from 7.79 vol.% (unaged) to 13.36 vol.% (RTFOT+PAV aged) – also mentioned
 19 amongst others in (17, 19, 28) – appears to be the only, or at least the most important consequence
 20 of aging on the microstructure of asphalt binder.
 21



22
 23 **FIGURE 5 Results from CR tests on unaged and RTFOT+PAV aged precipitated blends at +5°C. Creep**
 24 **compliance is shown in linear scale (left) and in logarithmic scale (right) for a better representation of creep**
 25 **curves with high asphaltene concentration.**

26 Based on the physico-chemical and microscopic analysis of the binder, a concept of the
 27 microstructure of asphalt binder is proposed in FIGURE 6 (left) consisting of a continuous matrix
 28 of maltenes with asphaltene inclusions. A structural concept of the representative volume element
 29 (RVE) for micromechanical modeling is shown in FIGURE 6 (right). An RVE of asphalt binder

1 has a continuous matrix of maltenes with spherical asphaltene inclusions. The network-like
 2 structure of shells around the asphaltenes is represented by an interaction phase appearing as
 3 needles with arbitrary orientation.
 4



5
 6 **FIGURE 6 Microstructural model (left) and micromechanical representation (right).**

7 With the micromechanical model (FIGURE 6), the viscoelastic behavior of the asphalt binder can
 8 be predicted, considering the aging-induced change of the material response due to increasing
 9 asphaltene concentration. For this, the identification of the model input parameters is a crucial
 10 task. The material properties of the maltene phase can be characterized directly by CR tests. The
 11 material behavior of asphaltenes, however, can be assessed indirectly by back-calculating from
 12 CR test results of precipitated blends. Likewise, the volume fraction of the interaction phase can be
 13 obtained. As outlined in (29), the power-law model, used to describe the mechanical behavior of
 14 asphalt binder and its constituents, is able to describe the experimentally obtained viscoelastic
 15 response very well. This implies a physically relevant form of Equation 2 according to (30),
 16 reading

17

$$J_{\text{mod}}(t) = J_0 + J_a \left(\frac{t}{\bar{t}} \right)^k \quad (2)$$

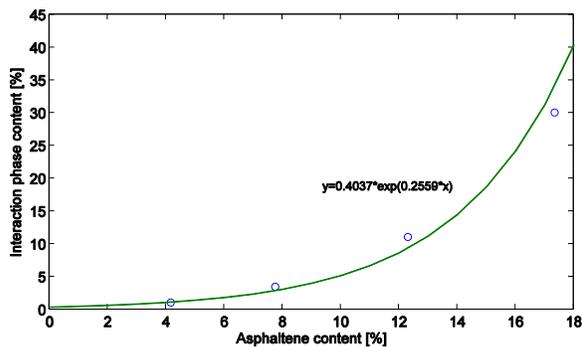
18 To identify the parameters $J_{0,malt}$, $J_{a,malt}$ and k_{malt} of the maltene phase, the error between
 19 experimentally obtained creep compliances J_{exp} from CR identification tests and predicted creep
 20 compliances J_{mod} is minimized through non-linear least square fitting. The obtained power-law
 21 parameters for the maltene phase at -5 °C, +5 °C and +15 °C are given in Table 2 describing almost
 22 perfect fits.

23 **TABLE 2 Power-law parameters for maltene phase at -5°C, +5°C and +15°C.**

	-5°C	+5°C	+15°C
$J_{0,malt}$ [1/MPa]	0.0980	0.2652	2.433
$J_{a,malt}$ [1/MPa]	0.0076	0.0766	1.205
k_{malt} [-]	0.8124	0.9386	1.027
R^2	0.99	0.99	0.99

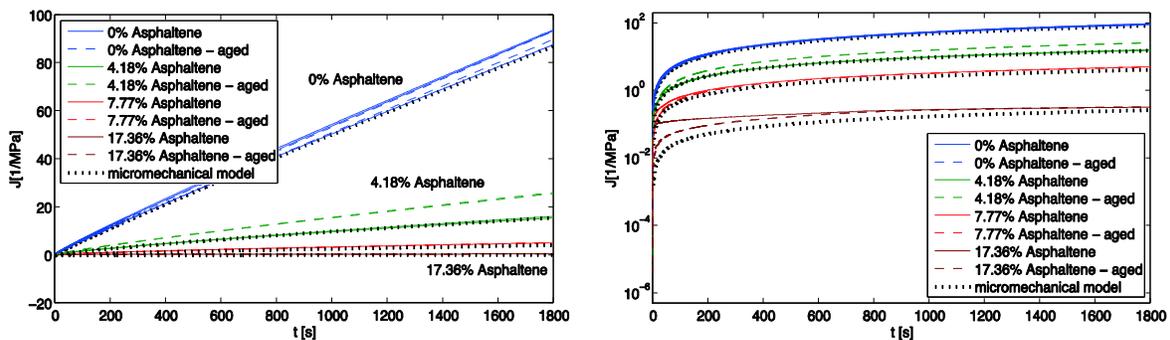
24
 25 As discussed above, power-law parameters of asphaltenes and the interaction phase are
 26 back-calculated from experimental results of precipitated blends with an asphaltene concentration
 27 of 4.18 vol.% at a temperature of +5 °C using the coefficient of determination R^2 as an indicator for
 28 the degree of accordance. Thereby it was determined that the parameters $J_{0,aspha}$, $J_{a,aspha}$ and k_{aspha} –
 29 applicable for asphaltenes as well as for the interaction phase – lie within a range, where their
 30 influence on the predicted material response can be considered insignificantly (31).

1 Since the needle-shaped interaction phase describes the structural influence of the asphaltene
 2 micelle network, its volume fraction f_{ip} is directly related to the asphaltene concentration. Similar
 3 to the power-law parameters, the volume fraction of the interaction phase f_{ip} is determined on a
 4 best-fit basis also employing R^2 to evaluate the degree of accordance. When correlating asphaltene
 5 and back-calculated needle content, an exponential relation can be found for (realistic) asphaltene
 6 concentrations up to 17.36 vol.% (see FIGURE 7). This is typical for e.g. molecular agglomeration
 7 processes in nature.
 8



9
 10 **FIGURE 7 Exponential relation between asphaltene and needle content (representing the interaction between**
 11 **micelle mantles).**

12 With all input parameters available, model predictions are compared to experimental results from
 13 aged precipitated blends with asphaltene concentrations of 4.18 vol.%, 7.77 vol.%, 12.32 vol.%
 14 and 17.36 vol.% in FIGURE 8. Besides the known volume fraction of the asphaltenes, the content
 15 of the interaction phase was the only parameter varied.
 16



17
 18 **FIGURE 8 Comparison of experimental results and micomechanical model predictions for precipitated blends**
 19 **at +5 C. Creep compliance is shown in linear scale (left) and in logarithmic scale (right) for a better**
 20 **representation of creep curves with high asphaltene content.**

21 To validate the proposed model CR tests were run not only on precipitated blends but also on
 22 original asphalt binders, including unaged, STA (RTFOT) and LTA (RTFOT+PAV) unmodified
 23 PG 58-22 samples with known asphaltene concentrations. The results can be seen in FIGURE 9.
 24

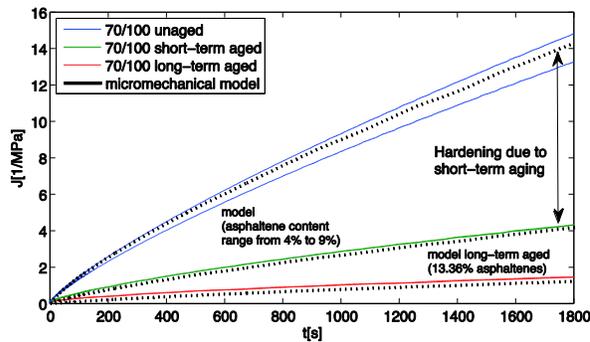


FIGURE 9 Comparison of experimental results and micromechanical model predictions for unaged, RTFOT- and RTFOT+PAV-aged asphalt binder PG 58-22.

The experimental results were related to model predictions taking the actual asphaltene concentrations into account. As can be seen in FIGURE 9, predictions of long-term aging (13.36 vol.% asphaltene concentration) fit experimental results very well. As described earlier, the binder samples have to be heated for the identification of the asphaltene concentration through n-heptane extraction. As the asphaltene concentration (n-heptane non-soluble phase) is strongly affected by heating due to aging, its determination is a challenging task. Especially for unaged and short-term aged samples, which are more susceptible to aging effects than already long-term aged samples, the reliable specification of the amount of asphaltenes is difficult. However, model predictions considering a realistic asphaltene concentration for unaged and short-term aged samples between 4 vol.% and 9 vol.% cover experimental results very well.

SUMMARY AND CONCLUSIONS

By interdisciplinary research into fundamentals of asphalt binder aging on physico-chemical and mechanical level, a microphysical and micromechanical model on binder aging was developed. The following conclusions can be drawn:

- Long-time (oxidative) aging of asphalt binder in the field may not only be triggered by atmospheric oxygen but also by other reactive gases like nitric oxides and ozone. These gases are available in much smaller concentrations but have a significantly higher oxidation potential than atmospheric oxygen at temperatures occurring in the field ($< +65^{\circ}\text{C}/150^{\circ}\text{F}$). Water soluble oxidants, like HNO_3 , H_2SO_4 or H_2O_2 can penetrate into binder and base layers and promote aging in these layers.
- A microphysical model on asphalt binder aging based on the idea of the micelle model explains long-term aging by oxidation through changes in the polarity distribution within matrix, mantle and micelle. An increasing gap in polarity due to oxidation may explain the macroscopic effect of increasing brittleness associated with binder aging.
- It was shown by AFM that precipitated blends produced from fractionated maltenes and asphaltenes exhibit a microstructural similar to the original asphalt binder. The presence of asphaltenes seems to be responsible for the formation of the "bee" structure or cantana phase.
- Mechanical analysis of precipitated blends with different concentrations of asphaltenes showed that by adding asphaltenes to the maltene phase, a network-like structure in the

- 1 asphalt binder is introduced. This strongly affects the mechanical behavior in terms of
2 increasing stiffness.
- 3 • Comparative mechanical analysis of precipitated blends from unaged and long-term aged
4 (RTFOT+PAV) samples indicate that the increase in asphaltene concentration with aging
5 is the only or at least the most important consequence of aging on the mechanical behavior
6 in terms of increasing stiffness.
 - 7 • A micromechanical model explaining the macroscopic, mechanical binder behavior based
8 on the behavior of maltene phase and asphaltenes was established. The mechanical
9 behavior of unaged, short-term and long-term aged asphalt binders can be predicted by
10 employing the model.

11 Acknowledgements

12 The authors would like to express their gratitude to the Austrian national research promotion agency (FFG) and the
13 industrial partners of the project "Oekophalt" for co-financing the research.

14 15 REFERENCES

- 16
- 17 1. European Parliament, *European Waste Framework Directive*, in 2008/98/EG. 2008:
18 Brussels.
 - 19 2. Huang, S.C., Pauli, A.T., Grimes, R.W. and Turner, F., *Ageing characteristics of RAP*
20 *binder blends - what types of RAP binders are suitable for multiple recycling?* Road
21 Materials and Pavement Design, 2014. **15**: p. 113-145.
 - 22 3. Ongel, A. and Hugener, M., *Aging of bituminous mixes for rap simulation*. Construction
23 and Building Materials, 2014. **68**: p. 49-54.
 - 24 4. Liu, G., Nielsen, E., Komacka, J., Greet, L. and van de Ven, M., *Rheological and chemical*
25 *evaluation on the ageing properties of SBS polymer modified bitumen: From the*
26 *laboratory to the field*. Construction and Building Materials, 2014. **51**: p. 244-248.
 - 27 5. da Costa, M.S., Farcas, F., Santos, L., Eusebio, M.I. and Diogo, A.C., *Chemical and*
28 *Thermal Characterization of Road Bitumen Ageing*, in *Advanced Materials Forum V, Pt 1*
29 *and 2*, L.G. Rosa and F. Margarido, Editors. 2010, Trans Tech Publications Ltd:
30 Stafa-Zurich. p. 273-279.
 - 31 6. Hagos, E.T., Molenaar, A.A.A. and van de Ven, M.F.C., *Chemical characterization of*
32 *laboratory and field bitumen aging in Porous Asphalt Concrete*. Advanced Testing and
33 Characterisation of Bituminous Materials, Vols 1 and 2, 2009: p. 173-184.
 - 34 7. Le Guern, M., Chailleux, E., Farcas, F., Dreessen, S. and Mabile, I., *Physico-chemical*
35 *analysis of five hard bitumens: Identification of chemical species and molecular*
36 *organization before and after artificial aging*. Fuel, 2010. **89**(11): p. 3330-3339.
 - 37 8. Poulikakos, L.D., dos Santos, S., Bueno, M., Kuentzel, S., Hugener, M. and Partl, M.N.,
38 *Influence of short and long term aging on chemical, microstructural and*
39 *macro-mechanical properties of recycled asphalt mixtures*. Construction and Building
40 Materials, 2014. **51**: p. 414-423.
 - 41 9. Allen, R.G., Little, D.N., Bhasin, A. and Glover, C.J., *The effects of chemical composition*
42 *on asphalt microstructure and their association to pavement performance*. International
43 Journal of Pavement Engineering, 2014. **15**(1): p. 9-22.

- 1 10. Fernandez-Gomez, W.D., Quintana, H.R. and Lizcano, F.R., *A review of asphalt and*
2 *asphalt mixture aging*. Ingenieria E Investigacion, 2013. **33**(1): p. 5-12.
- 3 11. Zhang, H.L., Yu, J.Y., Feng, Z.G., Xue, L.H. and Wu, S.P., *Effect of aging on the*
4 *morphology of bitumen by atomic force microscopy*. Journal of Microscopy, 2012. **246**(1):
5 p. 11-19.
- 6 12. Hofko, B., Blab, R., Eberhardsteiner, L., Fuessl, J., Grothe, H., Handle, F. and Hospodka,
7 M. *Impact of Field Ageing of Binder on Performance of Hot Mix Asphalt*. in *Proceedings*
8 *of the 12th ISAP Conference on Asphalt Pavements*. 2014. Raleigh, NC.
- 9 13. Petersen, J.C., Robertson, T., Branthaver, J.F., Harnsberger, P.M., Duvall, J.J., Kim, S.S.,
10 Anderson, D.A., Christiansen, D.W., Bahia, H.U., Dongre, R., C.E., A., Sharma, M.G.,
11 Button, J.W., and Glover, C.J., *Binder Characterization and Evaluation Volume 4: Test*
12 *Methods (SHRP-A-370)*, in *Strategic Highway Research Program*. 1994, National
13 Reserach Council: Washington, DC.
- 14 14. ASTM, *ASTM D 4124-01: Standard Test Methods for Separation of Asphalt into Four*
15 *Fractions*. 2001. p. 6.
- 16 15. Handle, F. *Bitumen Structure and Bitumen Ageing*. in *Proceedings of the 15th Austrian*
17 *Chemistry Days*. 2013. Graz, Austria.
- 18 16. Zellner, R., *Chemie über den Wolken: ... und darunter*. 2011: John Wiley & Sons.
- 19 17. Lesueur, D., *The colloidal structure of bitumen: Consequences on the rheology and on the*
20 *mechanisms of bitumen modification*. Advances in Colloid and Interface Science, 2009.
21 **145**(1-2): p. 42-82.
- 22 18. Redelius, P., *Asphaltenes in Bitumen, What They Are and What They Are Not*. Road
23 Materials and Pavement Design, 2011: p. 18.
- 24 19. Read, J. and Whiteoak, D., *The Shell Bitumen Handbook*. 5 ed. 2003, London: Thomas
25 Telford Ltd. 464.
- 26 20. Lesueur, D., *The colloidal structure of bitumen: consequences on the rheology and on the*
27 *mechanisms of bitumen modification*. Adv Colloid Interface Sci, 2009. **145**(1-2): p. 42-82.
- 28 21. Solaimany Nazar, A.R. and Rahimi, H., *Investiagtion on Agglomeration-Fragmentation*
29 *Processes in Colloidal Asphaltene Suspensions*. Energy & Fuels, 2009(23): p. 8.
- 30 22. Sheu, E.Y., *Physics of asphaltene micelles and microemulsions - theory and experiment*.
31 Journal of Physics: Condensed Matter, 1996. **1996**(8): p. 17.
- 32 23. Fawcett, A. and McNally, T., *Polystyrene and asphaltene micelles within blends with a*
33 *bitumen of an SBS block copolymer and styrene and butadiene homopolymers*. Colloid and
34 Polymer Science, 2003. **281**(3): p. 203-213.
- 35 24. Eyssautier, J., Hénaut, I., Levitz, P., Espinat, D. and Barré, L., *Organization of Asphaltenes*
36 *in a Vacuum Residue: A Small-Angle X-ray Scattering (SAXS) -Viscosity Approach at High*
37 *Temperatures*. Energy & Fuels, 2012. **26**(5): p. 2696-2704.
- 38 25. Pollack, S.S. and Yen, T.F., *Structural Studies of Asphaltics by X-Ray Small Angle*
39 *Scattering*. Analytical Chemistry, 1970. **42**(6): p. 7.
- 40 26. Tripadus, V., Popovici, M., Peticila, M., Craciun, L. and Muresan, O., *The study of diffusive*
41 *motion in bitumen compounds by quasielastic neutron scattering*. Physica B: Condensed
42 Matter, 2004. **350**(1-3): p. E455-E458.
- 43 27. Hofko, B., Blab, R., Eberhardsteiner, L., Füssl, J., Grothe, H., Handle, F., Hospodka, M.,
44 Nahar, S., Schmets, A. and Scarpas, A., *Microstructure and Rheology of Bitumen - Friends*
45 *or Foes?* Materials and Structures, 2014.
- 46 28. Grover, R.A., *Structural Characterization of micromechanical properties in asphalt using*
47 *atomic force microscopy*, in *Texas A&M University*. 2010, Texas A&M University: College

- 1 Station, TX. p. 104.
- 2 29. Aigner, E., Lackner, R. and Pichler, C., *Multiscale prediction of viscoelastic properties of*
- 3 *asphalt concrete*. Journal of Materials in Civil Engineering, 2009. **21**: p. 771-780.
- 4 30. Füssl, J., Lackner, R. and Eberhardsteiner, J., *Creep Response of Bituminous Mixtures -*
- 5 *Rheological Model and Microstructural Interpretation*. 2013.
- 6 31. Eberhardsteiner, L., Füssl, J., Hofko, B., Blab, R., Grothe, H., Handle, F. and Hospodka,
- 7 M., *Influence of Asphaltene Content on Bitumen Behavior - Experimental Investigation*
- 8 *and Micromechanical Modeling*. Materials and Structures, 2014.
- 9