Aging of Asphalt Symposium
Delft, the Netherlands September 17th 2014

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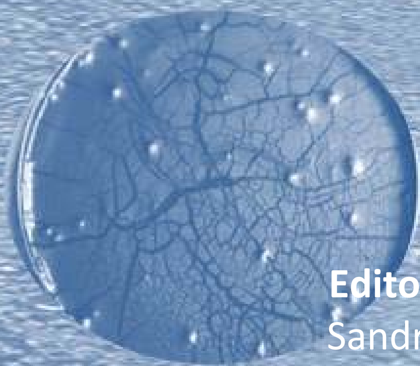

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Challenge the future

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1 Executive summary

Technical specifications for the asphalt concrete properties are developed to be able to specify mixtures that will perform well in pavement applications. Being able to identify and determine properties related to pavement performance in practice is crucial for both road authorities and contractors, since it allows for design and risk management by determining design life times and reliability. However, the properties of Asphalt Concrete (AC) change over its lifetime and since most pavement layers last for a decade or more these changes are crucial in determining the performance in practice.

For many of the standard materials the effect of aging is implicitly dealt with in the safety factors that also account for other effects such as the variation rest periods/healing and variations in traffic and weather in the design methods and specifications. Rapid changes in the materials used (increasing percentages reclaimed asphalt, bio-bitumen, rejuvenators, waste materials) and in the production of both bitumen (new refining methods resulting in different composition of bitumen) and asphalt concrete itself (warm mix asphalt, porous asphalt concrete, rubber asphalt mixtures) lead to increased uncertainty in the effects of aging. As a result, the uncertainties in pavement performance increase, which means the prediction of maintenance and the necessary budgets is getting more inaccurate.

In order to maintain the ability to reliably design and maintain pavements and determine the most cost-effective solutions for a given situation, a better understanding of the aging processes and objective methods to take into account aging effects on material properties is needed. This need is widely recognized, in the USA the Mechanical Empirical Design Guide takes aging into account through aging tests on the bitumen used and in Europe CEN TC227 works on establishing a method to assess the aging sensitivity of asphalt mixtures. This symposium aimed at combining the existing information and insights from ongoing research into recommendations that will allow the development of methods to determine aging sensitivity and the impact on pavement performance, facilitate the exchange of obtained data and stimulate further developments

The resulting recommendations are:

- Do make long term aging sensitivity of binders part of the bitumen standards and take the results from the aging sensitivity of binders into consideration when assessing AC properties. Be aware that RTFOT testing only gives an indication of the sensitivity of a penetration grade binder to aging during hot mix production and construction, it doesn’t work for hard grades, PMB’s or warm mixes.

- Because of the many variables involved, developing one test method to characterise aging sensitivity seems improbable. However, PAV aging is both practical and, if tests at various conditions are carried out, able to give kinematic properties. A PAV protocol for testing at two temperatures and time intervals could provide practical characterisation information for the short term and enable model development and validation on the long term. RCAT and other aging procedures could also be used in this sense, but considering the availability of equipment and the wide spread experience, PAV is the best candidate to allow the rapid development of international experience with the approach.
  Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and

CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100°C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

- Set-up and maintain field monitoring of temperature and UV radiation in various climate zones, as well as regular sampling over time and height to keep checking the predicted changes (from both tests and models), versus the actual changes in properties order to ensure reliability of the data as well as the applicability for pavement performance prediction. In setting up field tests, it is important to get both the composition of the virgin bitumen and the composition after mixing, transport and placement in the pavement. These compositions provide the starting points from both the material and pavement structure point of view and can be used to assess the development of aging products over time. There is a lot of discussion about the impact of binder recovery methods on the observed composition, so until it is proven that this does not have an influence, for comparisons the same recovery method should be used.

- Set up a coordination and support action on AC-Aging to continue to exchange information and experiences, both in research and in construction projects.

- develop an IR testing protocol, to facilitate the exchange of results and information.

- Compare the bitumen composition that is found through various recovery methods to establish if there is an effect and if so, develop a procedure to address this.

- To further understanding of aging, a Round Robin test on the differences in test conditions between US and EU, allowing better access to each other's data and knowledge would be useful.

- When developing aging tests for AC, it would be useful to look at the US experience. As long as there is no fundamentally correct method for assessing the aging, it would be preferable to standardize it as much as possible in order to allow cooperation and exchange of data.

2 Contents

Table of Contents

3 Introduction

3.1 Introduction to the symposium

The properties of Asphalt Concrete (AC) change over its lifetime. This is due to a combination of repeated traffic loads and the chemical and physical interaction between the material and its environment, such as moisture, oxygen and ultraviolet rays. The former, traffic related, change in properties is commonly referred to as fatigue. The latter, environment related change, is called aging.

Since most pavement layers last for at least 10 years, aging is an important issue in characterizing AC mixtures. If only properties of recently produced material are determined, this can lead to unrealistic expectations, both under or over-estimating the expected performance, in practice.

In the symposium a number of experts from various countries exchanged data, experience, knowledge and theories on aging of both bitumen (or asphalt) and AC. This document summarizes the background information, set-up and results from this symposium and aims to contribute to the development of an objective assessment of aging sensitivity of AC.

3.2 Structure of the document

In this document some background concerning the current requirements for aging assessment are given Chapter 4. Chapter 5 gives the list of participants and the symposium program. The summaries of the presentations and discussions are given in Chapter 6. In Chapter 7 the results from the overall discussion and the advice arrived at towards the end of the symposium are presented and finally, the copies of sheets the speakers used are included in Chapter 8.

4 Background on aging in specifications

4.1 The relevance of aging

The importance of aging in bituminous materials is based on the fact that most pavement damage occurs only after a considerable service life, from 10 to 20 years for surface layers to considerably longer times for binder and base layers, depending on the structural design approach used. The material properties change during this time due to aging, especially for the surface layers which are exposed to moisture, large temperature changes, oxygen and UV light. As a result, it are the aged material's properties that determine its sensitivity to damage. This means that o assess the suitability of a material for a given application, not just its original properties, but also some indication of how these properties change over time or an indication of a minimum performance that will be retained over time is needed. However, aging is a complex process, affected not only by the material characteristics, but also by the production and construction process and local environmental conditions and governed by chemical and physical relations that aren't known yet. Despite that, there are some test that are used to get an indication of the resistance to aging. In this chapter some of the common aging tests are described. It is by no means a complete list, the aim is to show examples of the current practice of dealing with aging in specifications as a background for the symposium content.

4.2 Aging tests: bitumen

4.2.1 Short term aging: RTFOT

Aging tests can be separated into tests on bitumen and tests on the asphalt mixture. For bitumen a common test to represent the short term aging of bitumen that takes place during mixing, transport and placement is the Rolling Thin Film Oven Test (RTFOT, AASHTO T240 [1],ASTM D 2872 [2] and EN 12607-1 [3]). Besides in the actual standards, descriptions of this test can be found in [4] and [5].

In this test bitumen is placed in glass bottles in a circular rack in a strictly specified oven.. The rack contains eight bottles in total with 35 grams of bitumen per bottle. The oven is heated to 163^{o}C before placing the bottles in the rack and they are left in the oven for 75 ([3]) or 85 (**Error! Reference source not found.** and [2]) minutes of testing. The rack rotates the bottles at a rate of 15 revolutions per minute while the oven is at a temperature of 163^{o}C. During the test air is being blown into the oven at 4000ml/minute, with the air-inlet such that it blows into each bottle at the lowest point in the revolution . After testing the mass loss, or more specifically the mass change (since some bitumen may increase in density due to oxidation), is determined. The fact that some bitumens increase in mass while others decrease, indicates that during the test both a loss of volatiles and increasing moleculair size due to oxidation occur. This was corroborated by a study [6] using inert gas, it that case it was found that only a mass decrease was measured.

4.2.1.1 USA

The material from two of the eight bottles is used to determine the change in mass, the material from the other bottles is used for DSR testing (T315 [7]) to obtain the G*/sinδ after short term aging, in the dynamic shear test which is used in AASHTO M320 [8], as part of the requirements for binders in performance graded binders. Alternatively, the material can also be aged further using the pressure aging vessel.

4.2.1.2 Europe

In Europe also, the mass loss is determined based on the average of two bottles. The additional material is used to determine the change in penetration, ring and ball temperature and viscosity at

60°C. The standards for penetration bitumen (EN 12591), polymer modified (EN 14023) and hard paving grade (EN 13924) bitumen specify requirements for the mass loss, change of penetration and/or the change in ring and ball temperature for most grades of bitumen. For soft binders (designed and specified by the dynamic viscosity at 60°C), the European standards specify the use of the Thin Film Oven (TFO, EN 12607-2 [9])instead.

4.2.1.3 Relation with field aging

In the BitVal project **Error! Reference source not found.** the aging procedures used in the European standard were investigated as a first step towards performance based binder specifications in Europe. The approach build on a large number of international publications, mostly from the USA and Europe.

In the project also the aging procedures were investigated. In case of the RTFOT different types of bitumen were used to make bitumen samples and asphalt mixtures, manufactured in different types of plants. The penetration at 25 °C, R&B softening point and ductility at 17 °C were determined for the bitumen before and after RTFOT and on the material taken from the coated materials. In the BitVal report **Error! Reference source not found.** it is concluded that:

- The bitumen source and the grade of the bitumen have a major role on the thermal susceptibility to hardening with coating.
- The manufacturing process and the composition of the asphalt mixture did not have a significant effect, on average, on the hardening of the bitumen in the experiment.
- The predictive capacity of the RTFOT method is satisfactory. In particular, it makes it possible to assess the change of R&B softening point with an acceptable precision.
- The RTFOT was a little more severe overall than mixing asphalt for the experiment conducted. Therefore, the RTFOT is a good method to indicate the risk of premature hardening of asphalt mixtures. Conversely, it will under predict the sensitivity to rutting.

More recently Besamusca et al. [10] concluded that RTFOT represents the aging due to mixing and such for penetration grade binders, but due to the fixed test temperature of 163 °C, it is not representative for hard grade, polymer modified and warm mix binders. For hard grade binders and polymers, this is probably because these materials do not mix as well as penetration binders. For warm mix binders, the test temperature is probably unrealistically high.

4.2.2 Long term aging: PAV

The pressure aging vessel (PAV, AASHTO R28 [11], EN 14769 [12]) is meant to simulate long term aging, the aging that occurs during the pavement service life. The current PAV test was developed during SuperPave **Error! Reference source not found.** as a modification of the aging vessel that had been in use in bitumen research for many years. In the current test, steel pans are filled with previously RTFOT aged bitumen that is then placed in a pressure vessels which is placed in an oven. The test uses both increased temperature and increased pressure to accelerate the aging. The aim is to achieve an amount of aging that is comparable to several years of service life in a pavement. In developing the test, bitumen reclaimed from field cores was used as a reference, using the bitumen from the whole core. More recent results indicate that the top part of field cores is aged much more than lower parts. This indicates that assessing the aging effect based on bitumen reclaimed from whole cores rather than only the top 1 or 2 centimetres underestimates the aging effect ([13], [14]). As such, PAV conditions are now thought to represent only limited aging times for the material at the top of a pavement. This appears to be true for most laboratory aging methods, Besamusca et al. [15] showed this for 70/100 bitumen in various (combinations of) lab tests compared to the aging in the field, the relative importance of aging due to production is, for bitumen 70/100 and porous asphalt concrete, considerably less important than predicted by the Shell bitumen handbook (Figure 2).

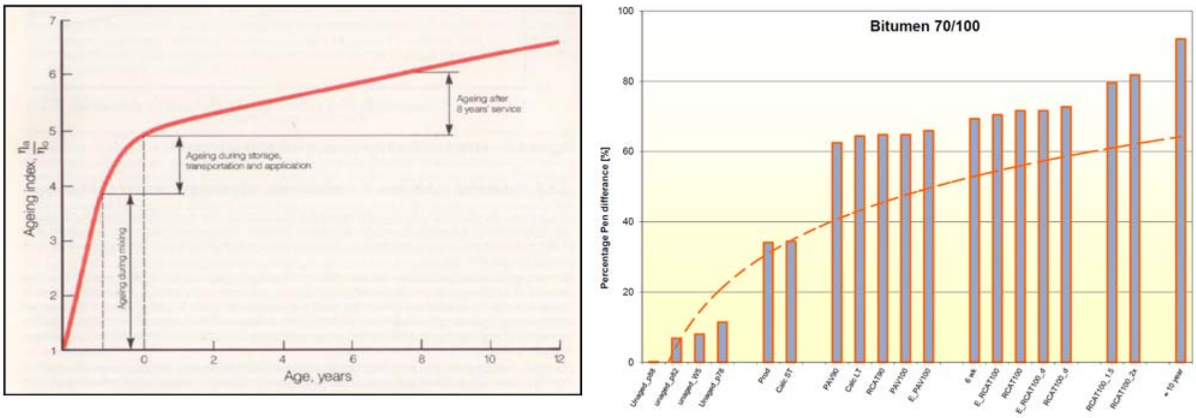

Figure 1: Aging effect graph from Shell (left) versus effect aging and various lab tests from Besamusca et al Error! Reference source not found. **(right)**

4.2.2.1 USA

In the USA, the PAV procedure entails ageing 50 g of bitumen in a 140 mm diameter container (giving a binder film that is approximately 3,2 mm thick) within the heated vessel, pressurised with air to 2,07 MPa for 20 hours at temperatures between 90 °C and 110 °C. The test takes 20 hour. Testing of the PAV (and RTFOT) aged bitumen in the DSR, bending beam rheometer and direct tension test is required for performance grading of bitumen.

4.2.2.2 Europe

In Europe the suggested sample size is the same as in the USA (50 grams in 140 mm containers, from the RTFOT (EN 12606-2), but different sizes containers are allowed as well. In case of a different size, the amount of binder must be adjusted to ensure a layer thickness of approximately 3,2 mm. The pressures and temperatures used overlap with those used in the standard used in the USA, but there are small differences, in Europe the pressure is 2,1 MPa (versus 2,07 in de USA) and the temperature range is 80^{o}C to 115^{o}C (versus 90 °C to 110 °C).
The current European bitumen standards do not require PAV aging or testing of PAV aged binder to assess the sensitivity to long term aging.

4.2.3 Rotating Cylinder Aging Test (RCAT)

The Rotating Cylinder Aging Test (EN 15323 [16]) uses a rotating flask with a bitumen layer at a specified temperature and oxygen flow for a fixed period of time. A grooved stainless steel rod of 34mm diameter is placed in the testing cylinder during the test. Typically, the effect of aging is assessed based on binder tests at the end of the procedure, but it is possible to take samples during testing in order to use a kinetic approach. The sample has a mass of approximately 650 grams, with a maximum of 900 grams.

Despite the versatility of the RCAT, RTFOT and PAV set-ups are more widely available and as such have become more or less the standard procedure for bitumen aging in Europe.

4.2.3.1 Short term aging

In case of short term aging, a temperature of 163^{o}C and a rotation speed of 5 rounds per minute are used. The air flow is 4 litres per minute. After the binder is placed in the set-up, it is allowed to heat up for half an hour without rotating or adding air. After that, the rotations and air flow are started and they continue for 235 plus or minus 5 minutes (circa 4 hours).

4.2.3.2 Long term aging

In long term aging, the test is performed at 90^{o}C. If the specimen was short-term aged using the RCAT, both the oven and the specimen (cylinder containing specimen is kept outside the oven) are allowed to cool down to the lower test temperature. Once the oven reaches the lower test temperature, this is maintained and the specimen is placed inside. It is left without rotations and airflow for half an hour.

If the specimen has had another kind of short-term aging, it is left in the pre-heated oven for one hour without rotating and airflow.

After this starting period, the sample is rotated at 1 round per minute and subjected to an oxygen flow of 4,5 litre per minute for 140 hours, plus or minus 15 minutes. During testing, usually at 17 and 65 hours, samples can be taken.

4.2.3.3 Aging of mastic

The RCAT can also be used to age mastic (defined as bitumen plus filler), added in the same ratio as used in the mixture. The amounts are determined in such a way that there is a total of 550 ml of mastic in the flask. For this test, the test cylinder, roller and the filler are pre-heated to 150^{O}C. The filler is placed into the cylinder and after homogenization the bitumen is added to it, the roller is placed in the cylinder and the whole system is put back in the oven. After the over temperature has stabilized, typically this takes 5 to 10 minutes, the rotation is started (1 round per minute), this is continued for 30 minutes. At the end of that period, samples are taken for mastic identification.
After this, either the procedure for short term aging (after heating the cylinder plus content to 170^{o}C) or that for long term aging (after allowing the cylinder plus content to cool to 90^{o}C) is performed.

4.3 Asphalt concrete

4.3.1 USA

In the SHRP A383 [17] report a short and long term aging procedures were tested on specimens and mixes with two different types of bitumen, two types of stone and two void percentages (4 and 8%, respectively). They tested extended mixing and short-term oven aging for loose mixtures and long-term oven aging, pressure oxidation aging and a low-pressure oxidation test in a triaxial cell for compacted specimens. They assessed the effect of aging by testing the modulus and determining the indirect tensile strength and peak strain. Since modulus testing is non-destructive, they tested the modulus on the same compacted specimen at various steps of aging, for the loose mixture and the destructive tests this is of course impossible so here also the variation between specimens plays a role. From the data, it seems that in most cases the stiffness and strength increase with aging while the strain at break decreases, which would be consistent with the expected increased brittleness due to aging. The study also refers to field validation tests, but the results are not included in the report.

In the study it is recommended to include a maximum exposure time in the short-term oven test for loose mixtures and to adopt an equiviscosity temperature for compaction of the aged mixture to prevent compaction effects from influencing the specimen properties. For specimen aging they recommend limiting the temperature in oven aging to 85°C (185°F). For the pressure oxidation tests, both with air and oxygen, they not a decrease instead of an increase in stiffness. This is attributed damage to the sample, which they call disruption due to the relieve of the gas pressure. As a result, they recommend low pressure or confined systems for aging cores. Their suggestions for aging of AC are:

- for short-term aging: oven-aging of loose mixtures at 135°C (275°F) for 4 hours
- for long term aging:
  - o dense mixtures: oven-aging of specimens at 85°C (185°F) for five days
  - o open graded mixes or mixes with soft binders: low-pressure oxidation (triaxial cell) technique at 85°C (185°F) for five days

In the MEPDG [18] ,which was published ten years later, the above procedures were not adopted. Instead, the effect of aging on the bitumen properties is determined using bitumen aging tests and this is related to the effect on the stiffness of the mixture through regression relations that take the mix composition into account (Figure 2).

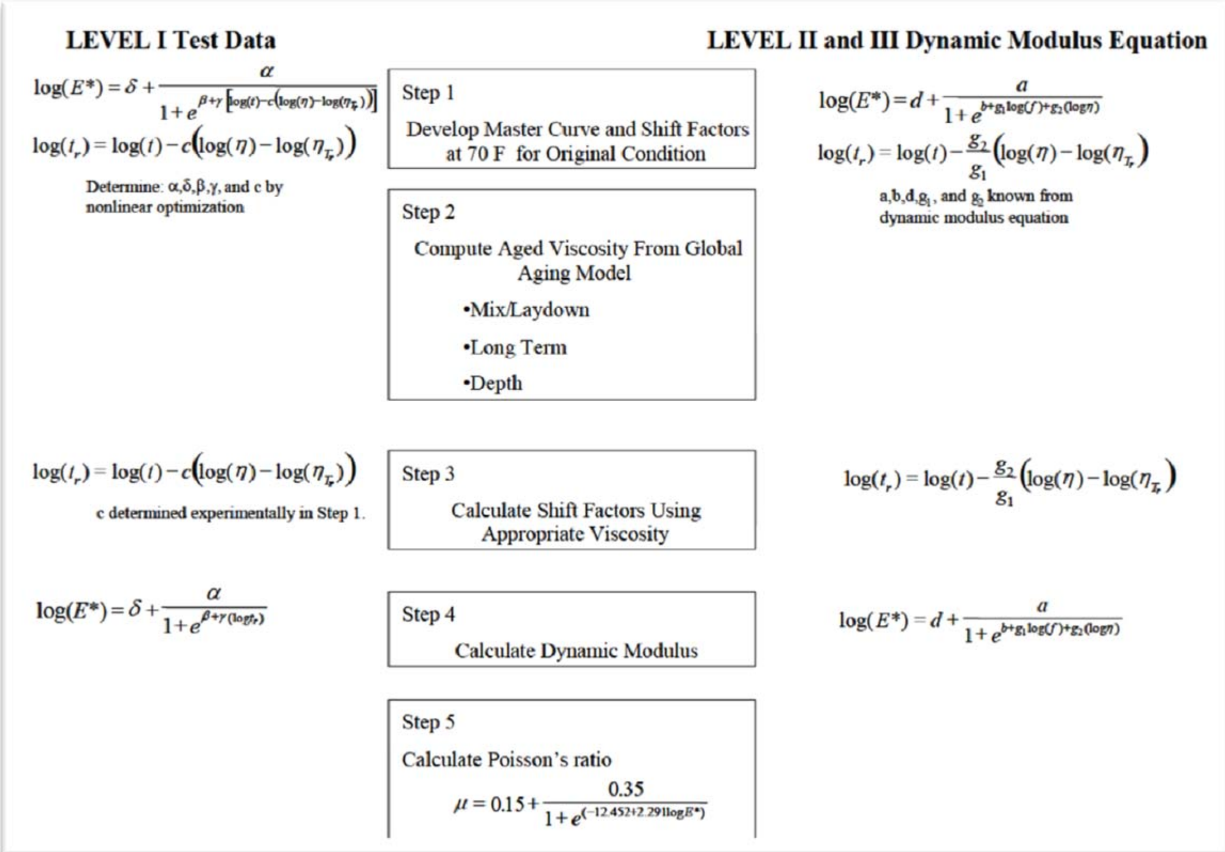

Figure 2: Aging of AC properties in the MEPDG works through regression based on bitumen aging (copy of fig 2.2.3 NCHRP 1-37A, Guide for Mechanical Empirical Design of New and Rehabilitated Pavement Structures, Final Report, Part 2- Design Inputs, Chapter 2 – Material Characterization, March 2004)

4.3.2 Europe

Although the current standards for Asphalt Concrete do not require either aging of the asphalt concrete itself, the CEN standards do provide tests for aging of AC. For example, CEN TC 227 is currently working on a draft standard which allows the assessment of the effect of oxidative aging of asphalt mixtures (prEN 12697-52:2014, [19]). This standard aims to provide methods for laboratory aging of both lose (pre-compaction) asphalt concrete and AC cores, either produced in in the laboratory or obtained from the field. The aged material can be used to make specimens and assess the effect of aging on the mixture properties or binder can be extracted from the aged AC to assess the effect of aging in the presence of filler and aggregates on binder properties.

When simulating short-term aging on the loose mixture, it is applied in a layer of 25±5mm, the temperature and conditioning time are not specified, but left to the individual member states to decide. However, it is advised not to take a conditioning temperature higher than the ring and ball temperature of the RTFOT aged binder, to prevent excessive draining of bitumen. It is noted that this temperature is on the safe side (i.e. low) and as an alternative determination of the softening point ring and ball on a homogeneous mastic of RTFOT-aged binder and filler (ratio of binder to filler according to the actual mix design) is mentioned. Also, there is a note referring to the SHRP-A-383 report and the conditions in it (135^{o}C for 4 hours). Obviously, there is a considerable difference between these suggested temperatures, which will lead to a lot of variation in testing and in results. With the large difference in suggested temperatures it may even lead to different mechanisms being tested.

The long term aging method for a loose AC mixture also only specifies the thickness in which to apply the mix and it includes the same note on choosing a test temperature that prevents excessive drainage, while at the same time other notes mention previous work by BRRC, RILEM and the university of Brunswig, using a PAV. They all use a similar approach but different temperatures and conditioning times. The BRRC ageing method sets a conditioning temperature of 60 C for 336 hours, the RILEM ageing method uses 85 C for 216 hours [20] and the Brunswig Ageing (BSA) method stores the specimens at 80 C for 96 hours and uses a pan with a perforated plate for improved airflow. The text for the concept standard also includes a note which states that PAV at 90^{o}C and 2,1 MPa for 20 hours gives comparable results to this RILEM protocol.

For aging of AC cores there are two approaches foreseen, one uses only temperature conditioning in an oven and is similar to the approach used by SHRP/AASHTO (which specifies a conditioning temperature of 85 C for 120 hours), the other involves forced flow with a gaseous oxidant. Although these aging procedures are based on research in one or more EU countries, the experience with them is still limited and the tests are not yet part of the CEN standards for asphalt concrete.

Besides this standard under development, there is also a test standard for hot mix asphalt saturation aging (SATS **Error! Reference source not found.**). This standard aims to assess the durability of adhesion in base and binder courses by aging specimens in the presence of water. The test is currently limited to mixtures with a binder content between 3,5 and 5,5% of 10/20 hard paving grade binder and air voids between 6% and 10%. In this tests five AC cores are first partially saturated (≤80%) by putting them in a vacuum desiccator covered with distilled water for half an hour at a pressure of 40-70 kPa. After this, the specimens are placed on different levels in the SATS set-up. The set-up is partially filled with water, causing one specimen to be under water and the other four at various heights above the water level. The specimens are left in the set-up at a pressure of 2,1 MPa and a temperature of 85^{o}C for 65 hours. The dynamic stiffness (using the indirect tension test, EN12697-26 Annex C) is determined before and after conditioning and the average of the stiffness ratios of the four specimens that were placed above water level are used to obtain the mixture stiffness ratio. Currently, this test is used in the United Kingdom. Experience with this test in other countries is very limited.

4.4 Literature

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5 Organisation of the symposium

5.1 Participants in the symposium

Name	Affiliation	role
Stavros Avgerinopoulos	De Montfort University	participant
Ronald Blab	TU Vienna	Speaker
Irina Cotiuga	Latexfalt	participant
Sandra Erkens	TU Delft/Rijkswaterstaat	Organizer/Chair
Ron Glaser	Western Research Institute	Speaker
Charles Glover	Texas A&M university	Speaker
Jaap van de Heide	Rijkswaterstaat	participant
Maarten Jacobs	BAM	Invited, unable to participate
Kim Jenkins	Stellenbosch University	participant
Diederik van Lent	TNO	Participant
Xueyan Liu	TU Delft	Participant
Bert-Jan Lommers	Latexfalt	Participant
Andre Molenaar	TU Delft	Participant
Steven Mookhoek	TNO	Participant
Sayeda Nahar	TU Delft	Participant
Marcus Oeser	TU Aachen	Speaker
Laurent Porot	Arizona Chemical	Speaker
Harry Roos	VBW	Invited, unable to participate
Tom Scarpas	TU Delft	Organizer/Chair
Alex Schmets	TU Delft	Participant
Hilde Soenen	Nynas	Speaker
Katerina Varveri	TU Delft	Participant
Martin vd Ven	TU Delft	Participant

5.2 Symposium Program

Tuesday 16/09/2014		
Arrival of international participants		
Wednesday 17/09/2014		
09:30 – 10:00	**Opening**	
09:30 – 09:45	Tom Scarpas	Welcome
09:45 - 10:00	Sandra Erkens	Setting the stage: Are current aging protocols capable of addressing field aging ?
10:00 – 12:15	**Session 1:**	
10:00 - 10:45	Charles Glover	Field Aging of Bituminous Materials and the Challenge of Laboratory Simulation
10:45 – 11:30	Ron Glaser	Advances in asphalt binder oxidation understanding with practical implications: Chemical and rheological behavior.
11:30 – 12:15	Hilde Soenen	What happens during aging and where is aging happening?
12:15 – 13:00	**Lunch**	
13:00 – 15:15	**Session 2:**	
13:00 – 13:45	Ronald Blab	How to understand field aging of bitumen - recent experimental and modeling efforts
13:45 – 14:30	Laurent Porot	Viscous to Elastic Transition: a way to qualify aging
14:30 - 15:15	Markus Oeser	Preventing Asphalt Binder Oxidation Using MMT-Nano-Particles
15:15 – 15:45	**Coffee Break**	
15:45 – 16:30	**Session 3:**	
15:45 – 16:30	Sandra Erkens	Discussion & drafting of conclusions and recommendations
16:30 -	Tom Scarpas	Closure
19:00 -	**Dinner**	

6 Symposium summary

The aim of this symposium is to combine as much of the existing knowledge and experience about asphalt concrete aging as possible, to provide an overview as well as a sound basis for current day decisions about sufficiently reliable aging tests as well as future research to further our understanding of the mechanisms involved. For that reason, the speakers that were invited cover the whole range, from binder to asphalt concrete aging, from chemical to mechanical properties, form laboratory to field experience and from models to collected data.

In this Chapter the contributions from the various speakers as well as the discussions that took place after their presentations are summarized. The slides they used can be found in Chapter 8, while the overall summary and conclusions are given in Chapter 7.

6.1 Charles Glover: Field aging of bituminous materials and the Challenge of Laboratory Simulation

6.1.1 Summary of presentation

Charles Glover considers aging a result from oxidation, over considerable depth. Oxidation causes binder embrittlement, changes rheology and fatigue resistance. He shows measurements and predictions of pavement temperatures at various levels, their model predicts temperatures very well. They use those temperature predictions as input for their kinetic oxidation model, which expresses oxygen absorption or viscosity as a function of aging time. The aging rate depends on temperature, he has data showing this effect and the relation between prediction and measurement.

Glover-Rowe parameter, G'/(n"/G') @15 ^{o}C and 0.005 rad/s is related to the ductility at 15^{o}C and 1 cm/minute, is based on the Maxwell model. As such it doesn't work for very ductile materials, but it does for more aged materials.
Charles is convinced that porosity doesn't play an important role, because there is plenty of oxygen present and it is replenished due to daily temperature changes. The relatively high aging rates in porous AC in the Netherlands would in that case be the result of relatively thin mastic layers, not the porosity in itself.

They use a pressure oxidation vessel, 3 month procedure. It can be used on the original binder to assess binder aging sensitivity, the effect on the binder rheology can be measured and the effect and rate of aging for that binder in the field can be predicted. The effect on AC properties is NOT in this method.

He shows a graph about POV and PAV aging versus field aging, quite a bit of difference but there are relations. The crucial step is relating the activation energy in the high pressure PAV to 1atm, which it is for field conditions. The advantage is that the PAV tests takes only a week. The parameter they use for aging is carbonyl content.

He indicates that the main challenge in taking aging into account involves finding a fast, practical aging test to determine a mixtures aging sensitivity. The actual aging will be location dependent, you could combine the local information with the measured sensitivity to determine suitability.

6.1.2 Discussion

Ron Glaser: PAV combined with RTFOT supposedly represents the real aging, but does it? In the data it looks relatively fresh. Is it severe enough?
Re: YES, especially for high temperatures such as in Texas RTFOT plus PAV underestimates the field aging, this is less of an issue for the Netherlands.
Irina Cotiuga: LATEXFALT research showed huge differences between laboratory and field aging
Ron Glaser: There are indications that the degree of oxidation for "short term aging" is not kinetically limited, but reactant limited and mostly happens because of the air in the loose mix voids. This air is rapidly consumed and this explains why warm mix resistance to rutting is generally not different from that of hot mix. Most of the oxidation occurs after leaving the drum, and its extent is limited by available air in the loose mix prior to compaction.

Andre Molenaar: Your approach is mostly focussed on oxygen, not on the effect of fines and such, did you look at that?
Re: a little works was done into filler effects on diffusivity, and this seems to match the theory. But there is not much data on this and no data at all about whether and is so how, coarser aggregates effect aging.

Sandra Erkens: You say porosity doesn't play a role if it is higher, yet we found that the aging of PA in the Netherlands is much more than your model would predict, how would you explain that?
Re: This t could be related to the thinner binder films, which would decrease the diffusion distance.
Martin van de Ven: That is partially in line with the results from asphalt on dikes, which after 30, 40 years still have penetration values of about 30, starting from pen 70/100. Those mixture have a high binder content (above 6%), but also a low porosity (around 4%). The low speed of aging is generally contributed to both these factors.

Irina Cotiuga: Did you try tests with thicker films in the PAV, to see if aging rate decreases.
Re: no, we used 3mm films in all tests, but we did vary specimen size.

6.2 Ron Glaser: advances in asphalt binder oxidation understanding with practical implications: chemical and rheological behaviour

6.2.1 Summary

Ron Glaser shows aged bitumen over specimen height for naturally aged ALF (the FHWA Turner Fairbanks accelerated loading facility) cores, they show a considerable variety over the height, with most of the aging at the top. The effect on the rheology is also considerable. Ron stresses the importance of gradients, temperature gradients are largest at the surface which means faster reaction rates. The temperature gradients over the pavement thickness leads to an aging and therefore a stiffness gradient. These ideas were developed based on observations of numerous field cores.

There is a need for field validation of laboratory studies and models, because in forensic studies, especially without the original materials, a lot remains unsure.

They studied chemical oxidation kinetics on 34 binders, using 50 micro meter film thickness at various temperatures. They combine a slow & fast reaction in their model, the generic form of the model is given in his slides. Their Arrhenius equation resulted in quite similar activation energies, which might indicate that the temperature characterisation is not necessary. Also, they found that this relation also works for PMB. He stresses that per binder you need only two oxidation points, four if you use pressure aging, to characterise a binder with respect to his model.

A plot of the change ins S=O + C=O versus Dlog10(Gc) shows linear relations per source (FTIR).
Ron explains that you can get your material's reaction rate from the intercept of the linear slope of the long term curve. But how do you quickly get those curves? One way is Pressurized Differential Scanning Calorimetry (PDSC).
Unfortunately, the aging mechanism appears to be more complex at higher temperatures and pressures. They now have a model that fits preliminary results through the range of temperatures and pressures. It looks like at higher T's sequential reactions take place. Their model includes different radicals, a small, active one (hydroxide i.e.), the other two are larger and not mobile at ambient temperatures.

6.2.2 Discussion

Hilde Soenen: how do you characterise naphthenic aromatics versus the others?
Re: Actually, we use SARA in our early data, now we use the more complete SAR-AD. Naphthenic aromatics decrease with oxidation and correlate to kinetically determined reactive material and master curve cross over parameter changes

Sandra Erkens: You mentioned the fact that PAV and RTFOT is not severe enough as a question to Charles after his presentation, do you have a solution?
Re: The PDSC method allows aging comparative up to 150 year old pavements (binder no longer solvable), it also has the advantage that it doesn't give you points, but a continuous curve. Longer PAV testing would also work and this wouldn't require new equipment. Whichever test you use, to moving toward predicting pavement performance, in my opinion, can only be done with oxidation kinetics characterization of the pavement bitumen. When you combine them with permeation and diffusion considerations to compute the oxygen gradients and thermal gradients and march those through time to get properties gradient which can be evaluated by FEM, you can get there.

Kim Jenkins: Did you do any work on chip seals, the aging there is quite severe?
Re: the seal is so thin that the diffusion path is very small and the UV becomes also important.
Irina Cotiuga*:* but the binder in seals is often not straight run.
Kim Jenkins: Quite often it is.
Martin van de Ven: the thickness is large compared to films in AC, but there is no filler, so less blockage of diffusion.

6.3 Hilde Soenen, what happens during aging and where is aging happening?

6.3.1 Summary

The presentation consist of three parts, the first focusses on laboratory aging with RTFOT+PAV, the second on field aging using recovered binders and the third on field aging of binder films.

Hilde discusses the rheological and chemical changes they found after these tests and she raises the question how important the aging temperature is. Nynas looked into various types of binders, to see if there was a difference in aging properties.
Hilde indicates that the aging index (defined as the ratio of original versus aged stiffness) is temperature and frequency dependent, with a more pronounced effect on the lower stiffnesss

values (the lower frequency/higher temperature range), as well as source dependent (i.e with respect to the. initial hardness).

They included visbroken binders in their research and they found these binders exhibit more sensitivity to fast aging. Also, due to RFOT and PAV aging the visbroken binders get a totally different fatigue slope (in DSR) while for straight run binders the fatigue lines shifts, but retain their slope.

They also looked into the effect of temperature on aging and aging products, comparing a straight distilled binder with an oxidized binder, binder aged using PAV and binder that is dark aged at room temperature:

- Room temperature aging only showed an increase in alcohols, no rheological change or change in molecular weight was found.
- PAV @ 60 and 100'C: showed an increase in carbonyl groups, poly aromatics and alcohols or sulfoxide as well as an increase in molecular weight and more structure in rheology.
- Oxidized bitumen: more poly aromatics, an increase in molecular weight and more structure in rheology

Furthermore, they looked into field aging in very old pavements *(Long Lasting Asphalt Pavements and Bitumen Ageing*, Xiaohu Lu , Per Redelius , Hilde Soenen , Mikael Thau, E&E conference 2012 and *Durability of Polymer Modified Binders in Asphalt Pavements*, Xiaohu Lu, Hilde Soenen, Serge Heyrman, Per Redelius, ISAP conference 2014) and there appears to be a clear relation between the air voids in the mixture and the reduction in penetration. This gives a clear indication that the mix composition affects aging and that binder aging alone is not sufficient to assess AC aging sensitivity. Comparing the effect on penetration and DSR stiffness (@10°C) with those of RTFOT and/or RTFOT&PAV aged samples indicated that RTFOT+PAV is representative for AC mixes with low void percentages, but it underestimates aging of more open mixtures.

Finally, they did tests with binder films exposed to climatic conditions, which resulted in much more change than RTFOT+PAV. Even in the lab, exposed to sunlight, but no other weather effect, the changes were considerable. The effect appeared to be about 120 micro meter deep.

They find that RTFOT+PAV are suited for dense materials (2-4% voids), assessing aging sensitivity in open pavements may need a longer laboratory aging time.
They suggest testing specimens that are aged as specimens to get information on which properties deteriorate first due to aging.

6.3.2 Discussion

Andre Molenaar: we tried to age PA samples, but they fell apart in the process. Yet, suppose I select an aging procedure that copies all the effects on the rheology, wouldn't that be enough? We did this for a PA mix and it corresponded with the FTIR and DSR of a 10 year old specimen from the road.
Re: Was it repeatable, or just fitting the aging to that specific core?

6.4 Ronald Blab: How to understand field aging of bitumen – recent experimental and modelling efforts

6.4.1 Summary

Ronald Blab presents the TU Vienna approach to understanding aging. It is based on the SARA-fractions, separating these fractions even further. They used Confocal Laser Scanning Microscopy, Atomic Force Microscopy, and Environmental Scanning Electron Microscopy to "look into" the bitumen. They consider the binder to consist of micelles in a matrix, which they link to the bees-matrix structure shown in AFM analyses of bitumen. TU Vienna used the fractioned components to create artificial bitumens, with known composition. They showed that there are no bees in the AFM if there are no asphaltenes in the binder, and with increasing asphaltene content, the number of bees increases.

For aging they distinguish three types of aging agents:

- UV and dust (surface active)
- NO_2, O_2, OH^- radical (reactive gasses, active in the top part of pavement)
- water soluble reactants (HNO, H_2SO_x, H_2O), active over the full pavement depth

They consider the matrix to be the part of the binder that is oxidized and they combine it with a recovering mechanism that is based on the reorganisation of the polar products, moving towards the asphaltenes, creating a highly polar micelle centre.

They work on a multi-scale model, based on mathematical formulations that allow them to upscale elastic and visco-elastic properties. They aged the components of their binder and added them, adding the same amount of asphaltenes, aged or not, resulted in the same response (stiffness), more asphaltenes gave stiffening/aging: therefore they conclude that aging is an increase in asphaltene content.

From field test they found that binder and base layers have the same rheological properties, very close to the properties directly after construction. Longterm aging appears to be restricted to the surface course.

In their experience, RTFOT matches well, chemically and rheologically, to short term aged material, RTFOT and PAV match rheologically, but not chemically to pavement conditions and it leads to SBS degradation.

They developed an alternative aging test, using corrosive gasses in a triaxial set-up. In the ITT you do see a stiffening effect, as well as in the DSR binder test. The test is performed at 60 ^{o}C and takes 4 days. Samples tested compare rheologically to RTFOT and PAV.

6.5 Laurent Porot, Viscous to elastic transition: a way to qualify aging

6.5.1 Summary

Laurent Porot states that with aging both the chemical composition and the properties change. In his presentation he discusses work they did to relate hardening of bitumen to changes in chemical structure that can be recorded through FTIR. For this, they looked at the cross over modulus (phase angle of 45 degrees), which can be seen as the transition of predominantly viscous to elastic response or vice versa.

In their study, Arizona Chemical looked at various bitumen grades, sources and aging levels as well as bitumen recovered from pavements. They tested them for penetration and ring and ball temperature, composition with FTIR and mechanical response using DSR.
They carried out their aging via PAV tests, repeating PAV aging cycles and sampling the bitumen between cycles for analyses. They found that PAV aging of the bitumen at 100^{o}C for 40 hours gave a similar pen to RAP (pen 15-20 [x0,1mm]). In their FTIR analyses they determined the area of the S=O and C=O over the C-H areas. In the DSR test they did a temperature sweep at a fixed frequency of 10 rad/s and looked at the cross-over properties (G* and T).

Plotting penetration versus softening point, like in the plot for the various binder grades, Laurent shows that all their results fall on more or less the same line, the binders from different sources, the different grades, the binders aged in consecutive PAV cycles and bitumen from RAP. The fact that the RAP binders fall around the line of the five PAV cycles indicates that these five cycles span field aging. However, it is not robust enough.Although there is a relation between the number of cycles and the age of the RAP it appears that the original composition of the bitumen also plays a role.

In the study, they looked into the Penetration Index as an aging indicator, but although PI increases with increased aging (more PAV cycles), when it is plotted against the ICO (area under the C=O peak in FTIR) the trend is not consistent.

They compared the C-H peak (area) for different binder grades from the same source and for binders of the same grade, but different sources. They found it was more or less constant. Similarly, they found that the cross-over temperature and G* are more or less constant for a given binder grade, even if the sources differ. For different grades of the same source, the cross-over temperature shifts while the stiffness remains around 10^7 Pa.
The ICO peak area increased consistently over the PAV cycles, ISO did not. Actually, ISO increased over the first few cycles and then it decreased and stayed more or less constant. When looking at ICO and ISO peak area values, the field samples mostly fell between 1 and 3 PAV cycles. The cross-over temperature increases with increasing PAV cycles, and G* decreases. The change in cross-over temperature is an indication of hardness and the change in cross-over modulus of temperature susceptibility. Thus, when the material ages it both hardens and becomes less temperature susceptible, resulting in a more elastic behavior at a wider temperature range

From their testing program they suggest plotting the cross-over modulus versus ICO, indicating that bitumen with ICO less than 0,05 and G* of $1x10^7$ Pa or more are non-aged, ICO between 0,02-0,12 and G8 between $3x10^6$ and $1x10^7$ Pa is aged and bitumen with ICO> 0,05 and G* less than $3x10^6$ is overaged. This could be used to assess RAP suitability of re-using in AC mixtures.

6.5.2 Discussion

Ron Glaser: This approach is useful for assessing RAP quality or monitoring pavements for remedial action. I prefer using cross-over, it is much simpler.
Sandra Erkens: but sometimes we see that the rheology matches, but chemistry doesn't, and that worries me.
Charles Glover: what matters is not so much the rheological state at failure, but how long it takes a material to get there.
Ron Glaser: adding fresh binders is mostly physical blending, rheology is the important parameter for that.

6.6 Marcus Oeser: Prevention of Asphalt Binder Oxidation using MMT-Particles

6.6.1 Summary

At TU Aachen they used montmorillonite (clay) nano particles to modify bitumen. In penetration binders this causes an increase in penetration and a decrease in $T_{r\&b}$ ("aging" like changes), with increasing mixing time (i.e. 2-150! minutes). With PMB this does not happen. For mixing times up to 30 minutes the effect is small.
The idea is that the MMT particles, which are plate like in shape, can act as "screens" or radiation/diffusions retarders in the mastic.

For 10% MMT the reduction of aging in RTFOT+PAV is more than the increase due to the MMT. The effect on adhesion, AC properties and binder chemistry still needs to be addressed.

6.6.2 discussion

Charles Glover: did you measure oxidation directly?
Re: no only, indirectly through rheology.

Ronald Blab: how does the ozon aging effect the chemistry?
Re: according to the chemists involved, it is closer to the field values than those from PAV aging.

Kim Jenkins: were the models you developed for a specific tests and how would they respond to a different type of test?
Re: the creep recovery tests were used for fitting the model.

Martin van de Ven: is the thickness and i.e. void content specified in the ozon aging test?
Re: not, it is just a prototype.

7 Conclusions, discussion and advice

7.1 Summary and conclusions

In the general discussion at the end of the symposium, the following topics were addressed:

7.1.1 RTFOT for short-term (production and construction) aging?

The participants agree that RTFOT tests provides a good indicator of bitumen aging sensitivity for binders used in HMA. For different types of production, other tests or test conditions may be needed.

However, the test does not give a prediction of field aging, because that strongly depends on mix composition and production effects (i.e. temperature). When using two different bitumens in exactly the same mix and using exactly the same production conditions, the bitumen that showed the most aging in the RTFOT will age most during actual production and construction, it is a sensitivity indicator and its relevance in relation to other factors like the type of filler are not well established.

7.1.2 PAV for binders?

PAV aging also doesn't provide an indication of binder field aging. In this case that is more serious, since the test is supposed to do just that. Many field results shown in this symposium (and in literature) show more aging than we get from PAV. Although true prediction of field aging is unlikely, for the same reasons as with RTFOT, capturing the right phenomenon is crucial.

Some participants indicate that in order to get a quick test ,we increased the temperature and pressure too much. As a result, we are not covering the actual phenomenon that occurs in the field, or at least not sufficiently. This suggestion has been made before, for example SHRP advices to use a temperature between 90-110 ^{o}C to compensate for PG grade, it is worthwhile considering such a recommendation for the temperature in the CEN test.

A useful alternative approach to trying to get a single test that represents all variables in practice seems to be using the test to capture the aging sensitivity of the bitumen. This would require doing the test at two temperatures and two time intervals per temperature (i.e. four tests to characterize a bitumen) in order to be able to determine kinetic information. This information could then be used in models that take into account mix composition and local climate conditions in predicting pavement aging.
Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100^{o}C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

7.1.3 Aging for AC?

There is general agreement that aging for AC is important, especially for (low temperature) cracking, ravelling and fatigue resistance. Comparing fresh AC mixtures will not give a reliable indication of the field performance for those properties. Also, even if both short and long term aging sensitivity of the binder is known, the aging sensitivity of the AC depends also on many other variables such as:

the mix composition (more voids and/or thinner binder films result in more aging under the same conditions and also the composition of the aggregate, or at least the filler, appears to have an effect) and climatic conditions (higher temperatures add to aging, so does UV light, at least on the surface and also water and/or moisture seems to have an effect).

However, if there is not yet a single test that can predict field aging of binders, it will be very difficult to come up with a test that will manage this for AC. So how do we relate the AC properties of fresh material to those of the aged material? Even if we could relate changes in chemistry/oxidation and rheology to their effect on the mixture properties, we would also have to know how the climatic conditions would affect the chemical changes. For AC a two step approach seems necessary, determine the mixture sensitivity to aging, for example through 4 PAV tests on the mixture or, as mentioned in Section 7.1.2, on bitumen to determine the kinetic information. This could then be the end result, an indication of the aging sensitivity, or it could be used in a model that describes chemical changes due to aging as a function of the climatic conditions and mix micro structure (porosity, film thickness) to predict the aging of a given mix in a specific climate (Figure 3).

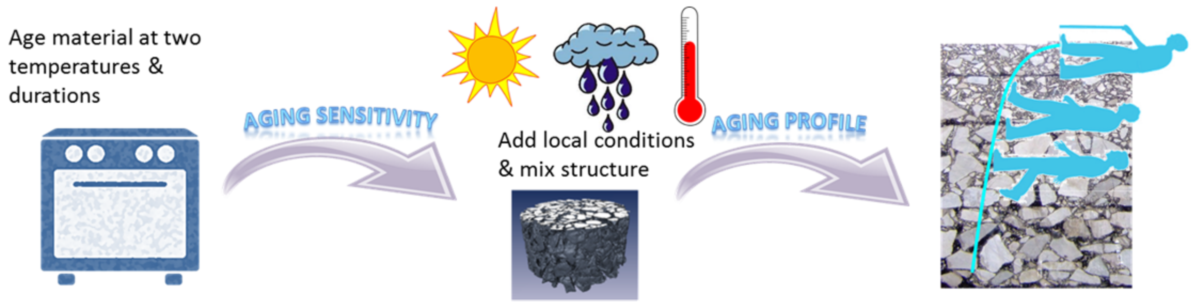

Figure 3: Two step approach to determining the aging of Asphalt Concrete

This would still require also assessing the effect of several levels of aging on the mechanical properties, but it would provide a robust system that also allows the assessment of aging of new materials In the laboratory uniformly aged specimens (or specimens made from aged material) can be tested and those properties can be used to ascribe properties to the material at various aging levels. Linking those properties to the ageing profile will eventually allow the analysis of pavements in time.

A simpler alternative, at least for the short term, could be the approach used in the MEPDG in the US, where standardised aging protocols are used to age specimens and there are requirements for the fresh as well as the aged material. In a given climate region, pavements that are near failure could be sampled to assess what the requirements for that type of mix in that climate zone should be.

7.1.4 General issues

There is no standard for Infra-Red measurements, which would be useful in case of standardisation of aging. It would at least ensure that the chemical composition information that is obtained can be compared between labs and countries.

The increase OH-groups/alcohol in bitumen over time is not covered by any of the current tests, this is something to keep in mind.

7.2 Recommendations

- Do make long term aging sensitivity of binders part of the bitumen standards and take the results from the aging sensitivity of binders into consideration when assessing AC properties.

Be aware that RTFOT testing only gives an indication of the sensitivity of a penetration grade binder to aging during hot mix production and construction, it doesn't work for hard grades, PMB's or warm mixes.

- Because of the many variables involved, developing one test method to characterise aging sensitivity seems improbable. However, PAV aging is both practical and, if tests at various conditions are carried out, able to give kinematic properties. A PAV protocol for testing at two temperatures and time intervals could provide practical characterisation information for the short term and enable model development and validation on the long term. RCAT and other aging procedures could also be used in this sense, but considering the availability of equipment and the wide spread experience, PAV is the best candidate to allow the rapid development of international experience with the approach.
  Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100^{o}C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

- Set-up and maintain field monitoring of temperature and UV radiation in various climate zones, as well as regular sampling over time and height to keep checking the predicted changes (from both tests and models), versus the actual changes in properties order to ensure reliability of the data as well as the applicability for pavement performance prediction. In setting up field tests, it is important to get both the composition of the virgin bitumen and the composition after mixing, transport and placement in the pavement. These compositions provide the starting points from both the material and pavement structure point of view and can be used to assess the development of aging products over time. There is a lot of discussion about the impact of binder recovery methods on the observed composition, so until it is proven that this does not have an influence, for comparisons the same recovery method should be used.

- Set up a coordination and support action on AC-Aging to continue to exchange information and experiences, both in research and in construction projects.

- develop an IR testing protocol, to facilitate the exchange of results and information.

- Compare the bitumen composition that is found through various recovery methods to establish if there is an effect and if so, develop a procedure to address this.

- To further understanding of aging, a Round Robin test on the differences in test conditions between US and EU, allowing better access to each other's data and knowledge would be useful.

- When developing aging tests for AC, it would be useful to look at the US experience. As long as there is no fundamentally correct method for assessing the aging, it would be preferable to standardize it as much as possible in order to allow cooperation and exchange of data.

TU Delft Delft University of Technology

Challenge the future

8 Presentations

8.1 Charles Glover, Texas A&M , An Asphalt Oxidation Perspective on HighRAC Mixtures

Field Aging of Bituminous Materials and the Challenge of Laboratory Simulation

Charles J. Glover
Artie McFerrin Department of Chemical Engineering
Texas A&M University/Texas A&M Transportation Institute

Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

2

Background

- Pavement binders oxidize and harden over time
  - A ***relentless process***
  - Occurs ***well below the immediate pavement surface***
  - Hardening ***results in binder embrittlement***: fracture at a lower strain
- Long-term goal has been to understand this process quantitatively and its ***impact on pavement durability, specific to each binder and pavement site*** – ***a 25-year effort***

Texas A&M Transportation Institute

Charles J. Glover
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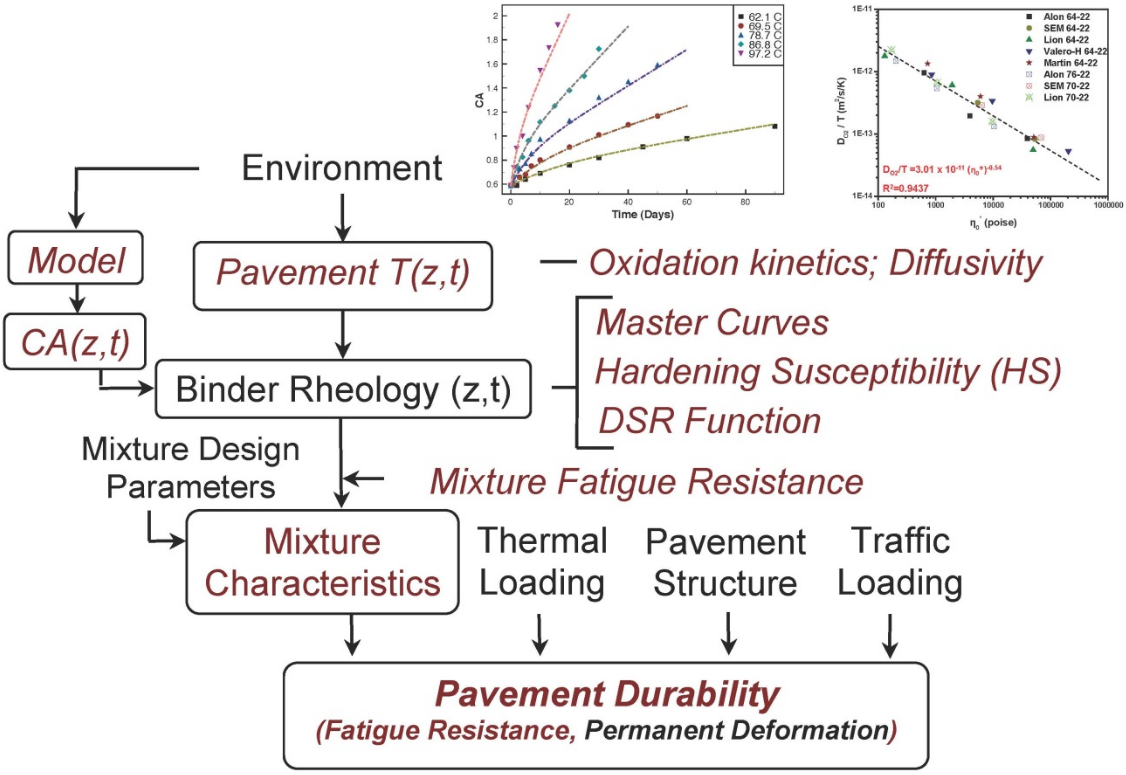
Artie McFerrin Department of CHEMICAL ENGINEERING

3

Pavement Performance Modeling



CJG, Delft-9-17-2014

4

Objectives

- To review some of this 25-year history, showing some details but **emphasizing the Big Picture:**
  - to predict pavement performance – ***design***
  - To show how any pavement can be a low-cost, effective, and efficient test section – ***forensics***
  - To provide an aging/durability test – ***fast aging test***

Texas A&M Transportation Institute

Charles J. Glover
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Artie McFerrin Department of CHEMICAL ENGINEERING

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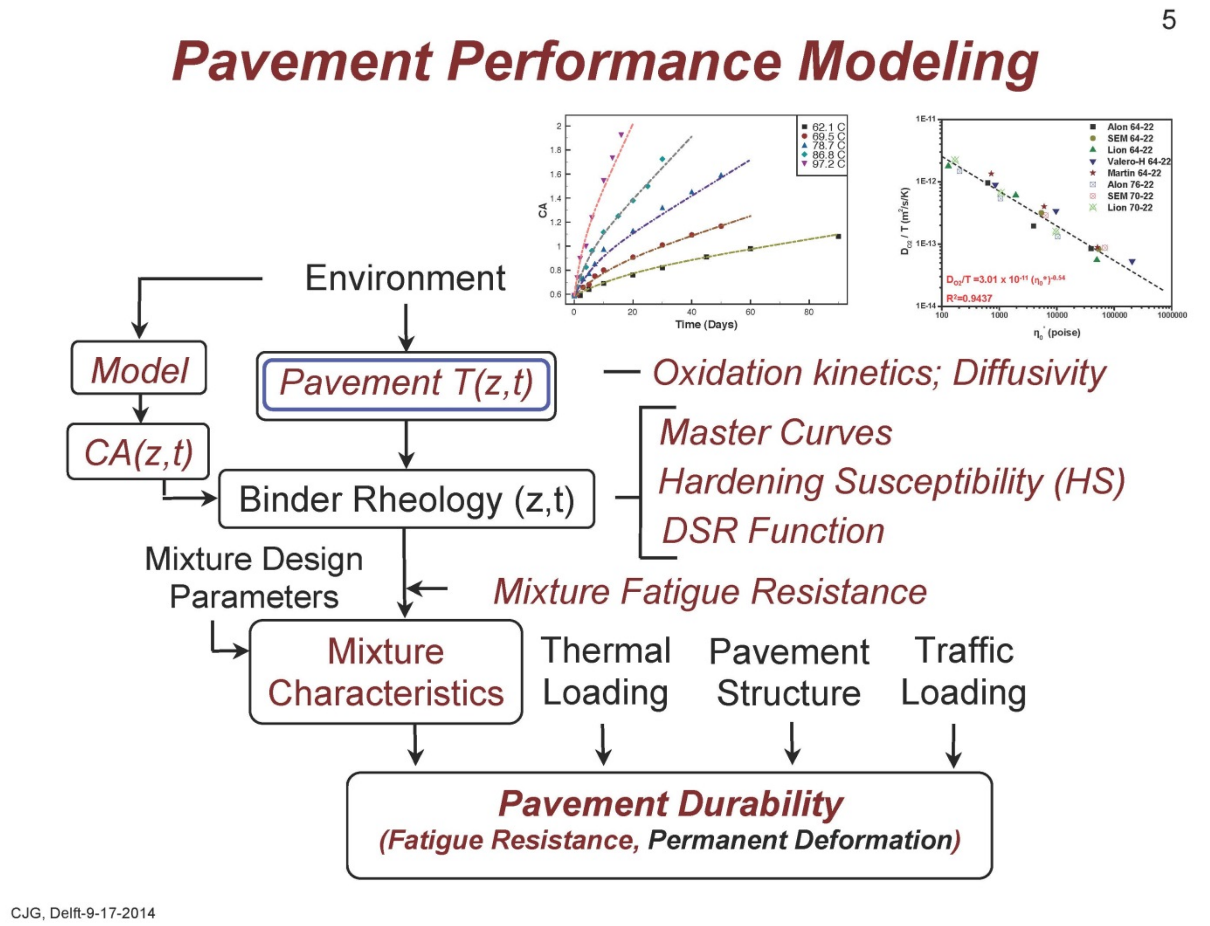
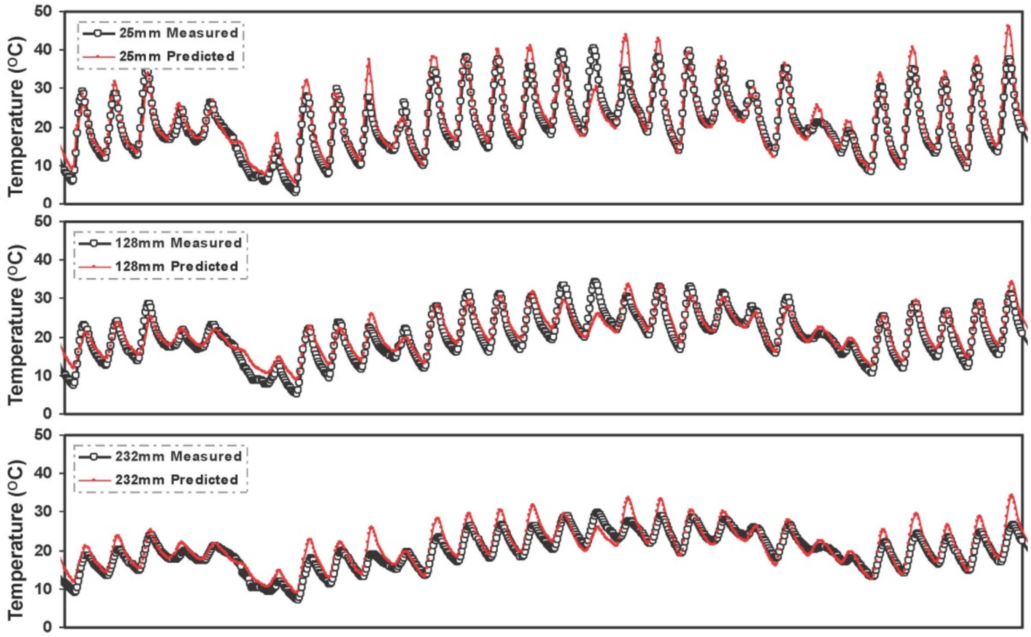


6

Temperature Calculations



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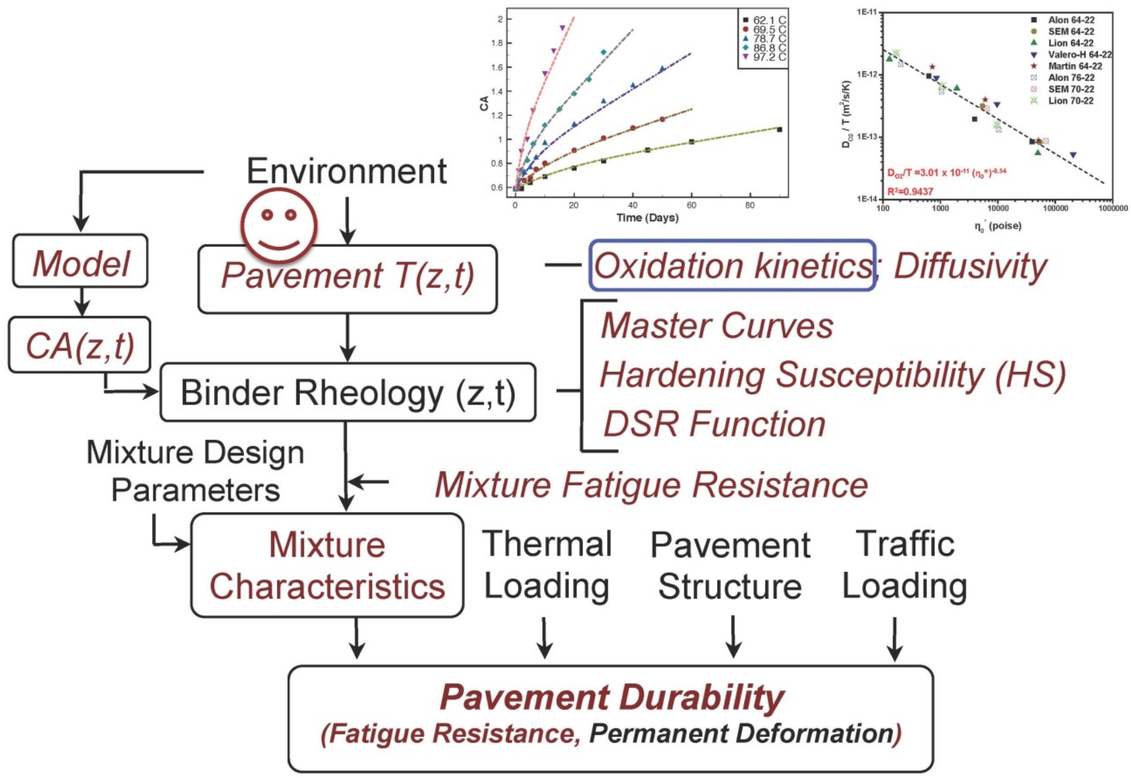
Pavement Performance Modeling



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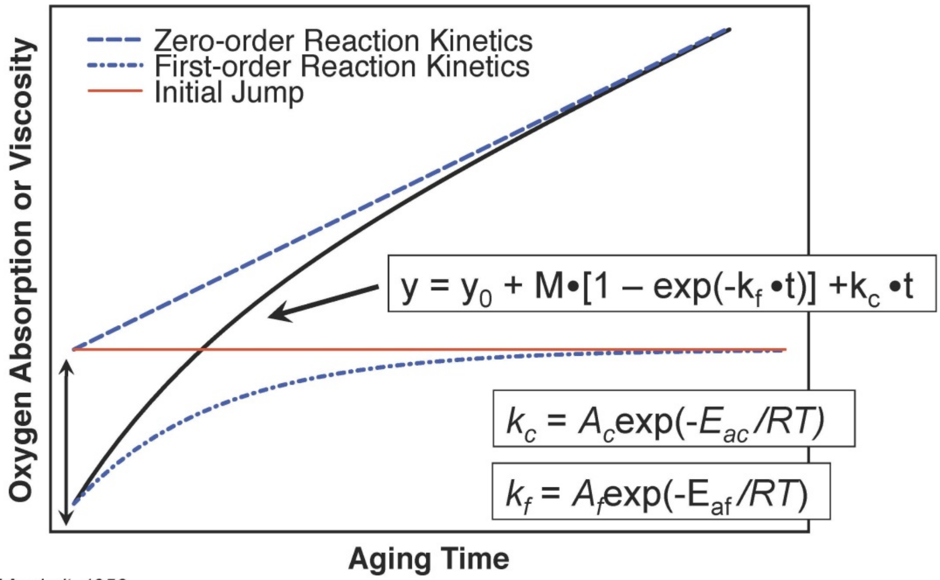
Background: Oxidation Kinetics



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Herrington, P.R. *Petroleum Science and Technology, Vol.16, 1998*

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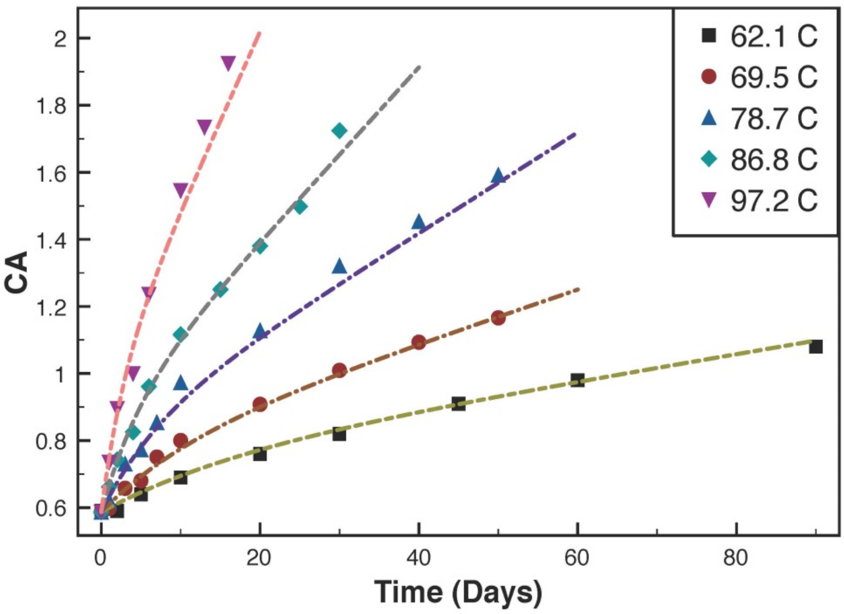
9

Oxidation Kinetics Data using Original Binder – 3 mos aging



Jin et al. (2011)

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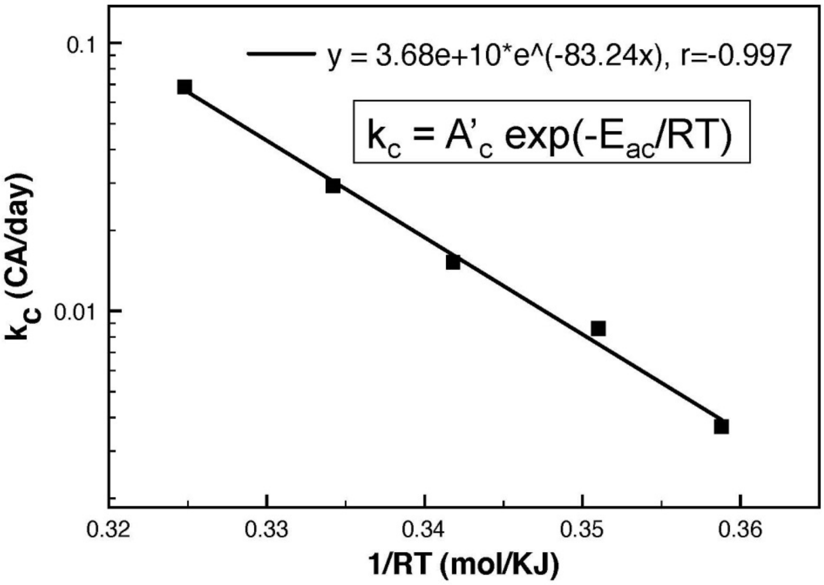
10

Constant-rate Reaction Kinetics



Jin et al. (2011)

$$CA = M \bullet [1 - \exp(-k_f \bullet t)] + CA_{tank} + k_c \bullet t$$

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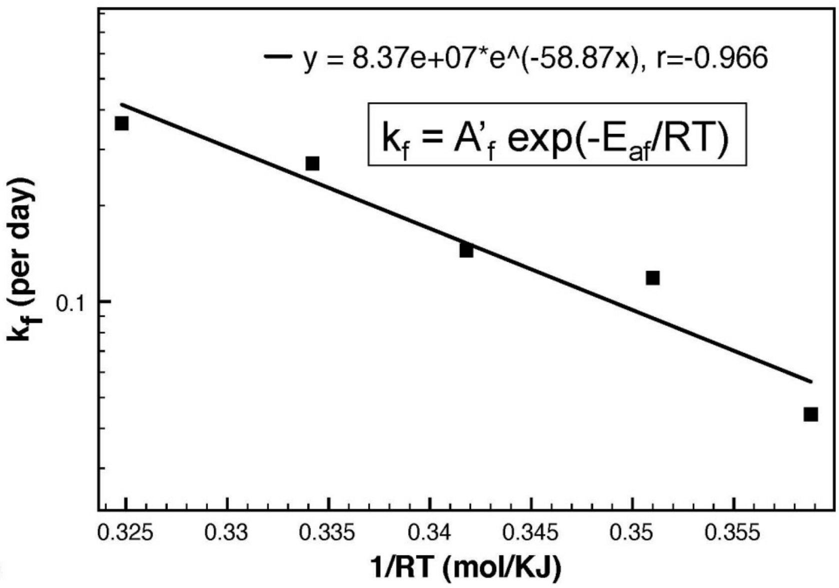
Fast-rate Reaction Kinetics



Jin et al. (2011)

$$CA = M \bullet [1 - \exp(-k_f \bullet t)] + CA_{tank} + k_c \bullet t$$

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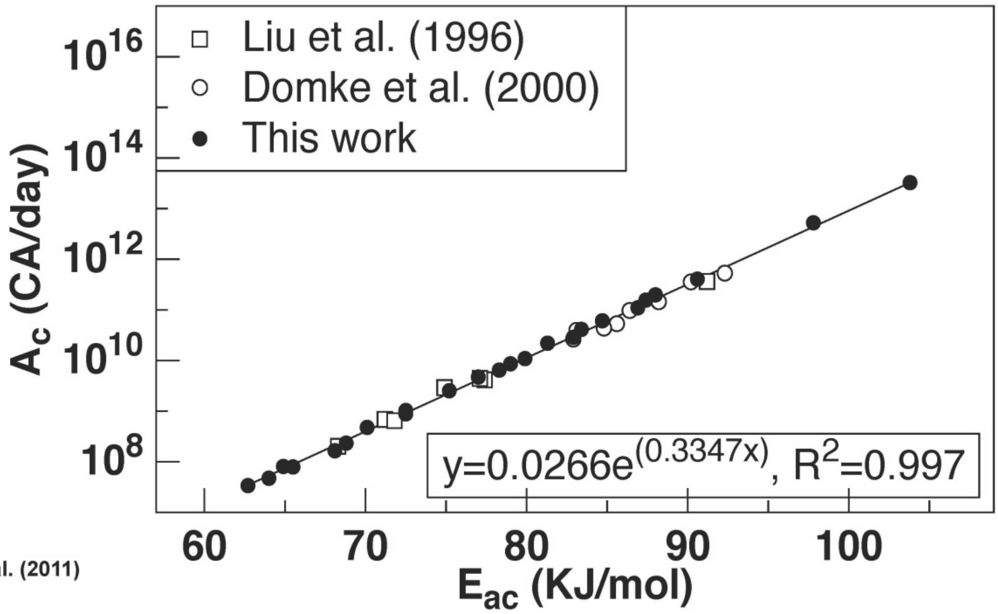
12

Kinetics Correlations



Jin et al. (2011)

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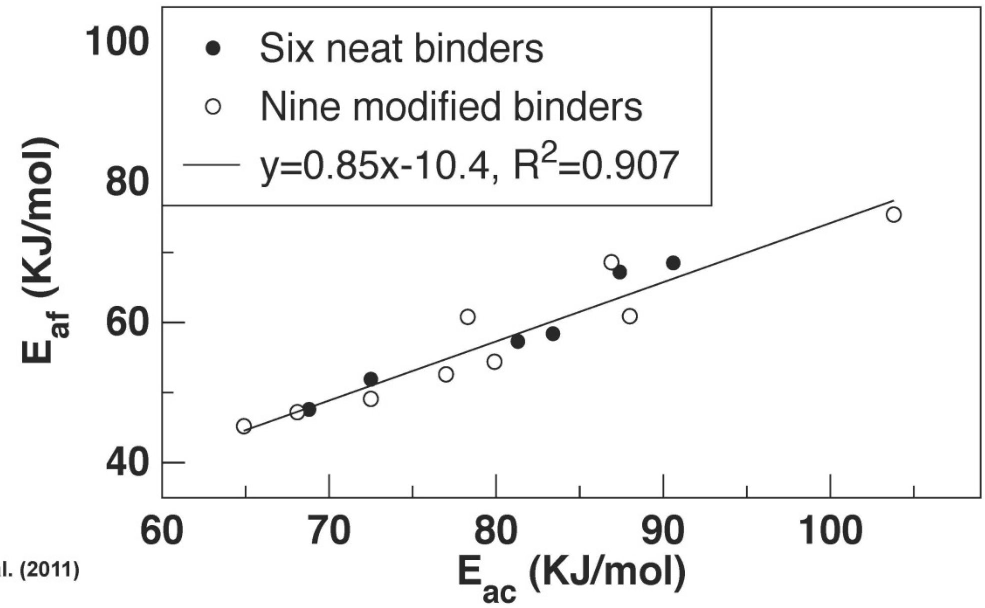
Kinetics Correlations



Jin et al. (2011)

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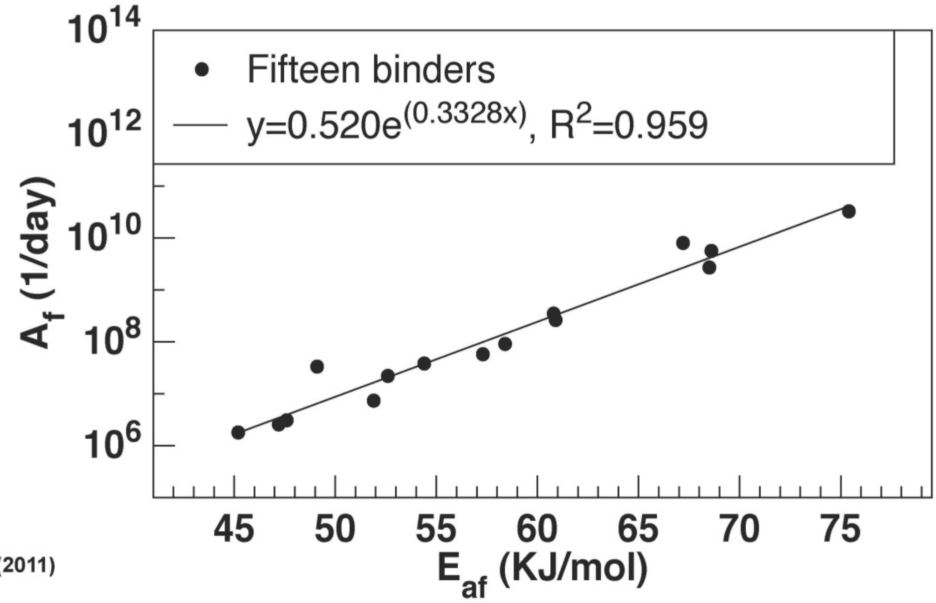
Kinetics Correlations



Jin et al. (2011)

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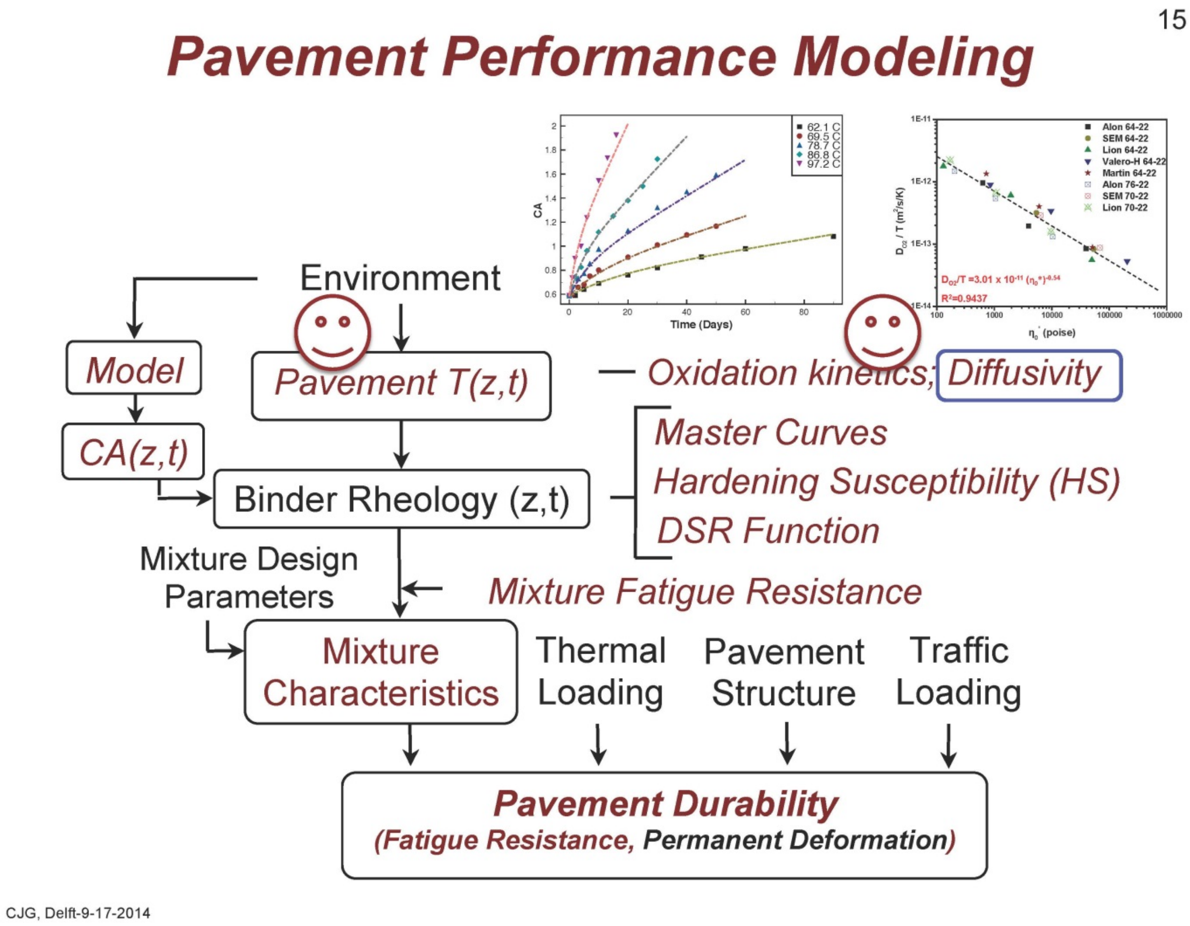
15
Pavement Performance Modeling
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
CA
Time (Days)
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
$D_{O2}/T = 3.01 \times 10^{-11} (\eta_0^*)^{-0.54}$
R^2=0.9437
D_{O2} / T (m²/s/K)
η_0^* (poise)
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Master Curves
Hardening Susceptibility (HS)
DSR Function
Binder Rheology (z,t)
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
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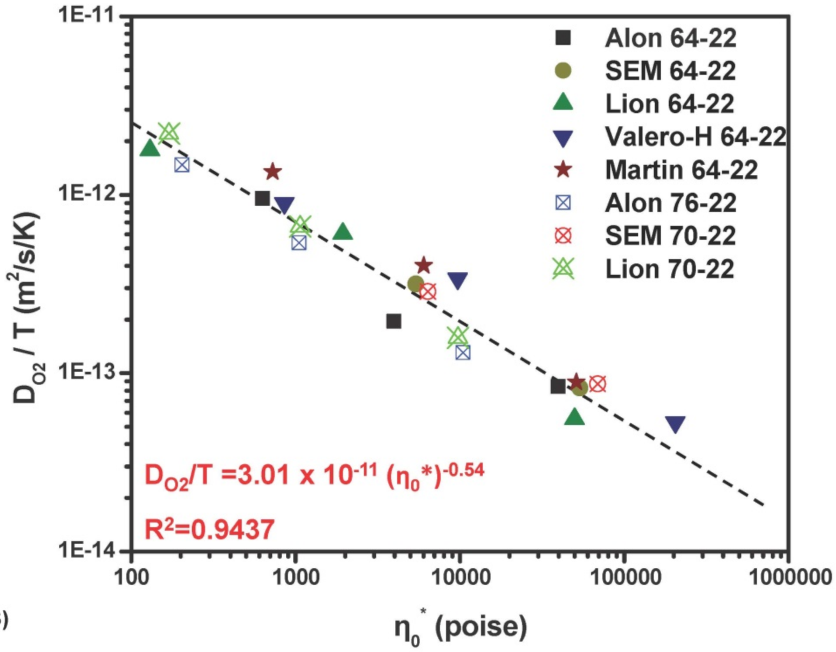
Background: O_2 Diffusivity in Asphalt



Han et al. (2013)

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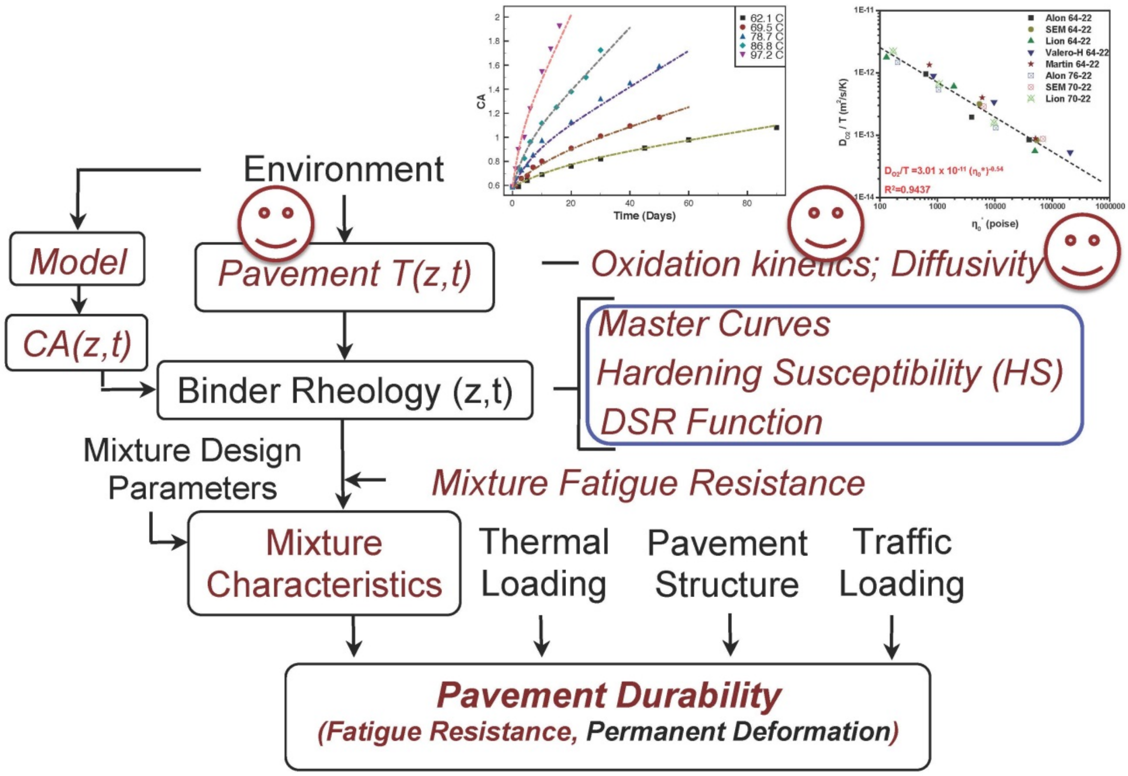
Pavement Performance Modeling



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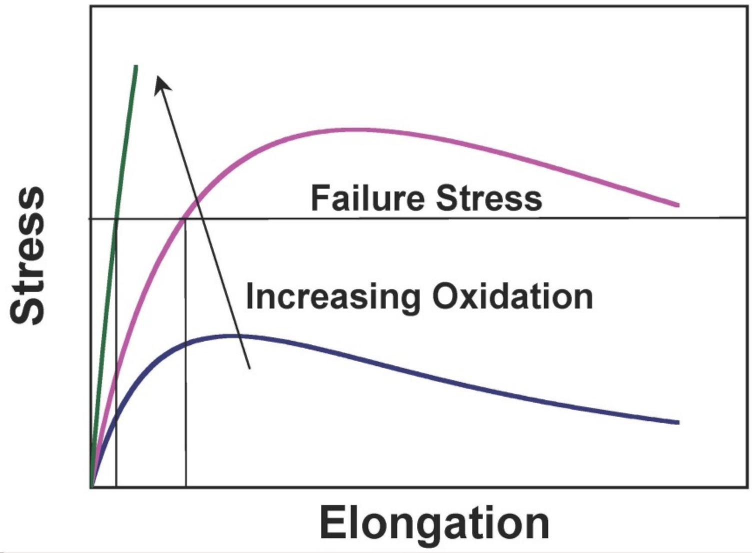
Background – A Key Concept: Binder Embrittlement

IN SERVICE, BINDERS OXIDIZE, BECOME STIFFER AND LESS DUCTILE…A RELENTLESS PROCESS!



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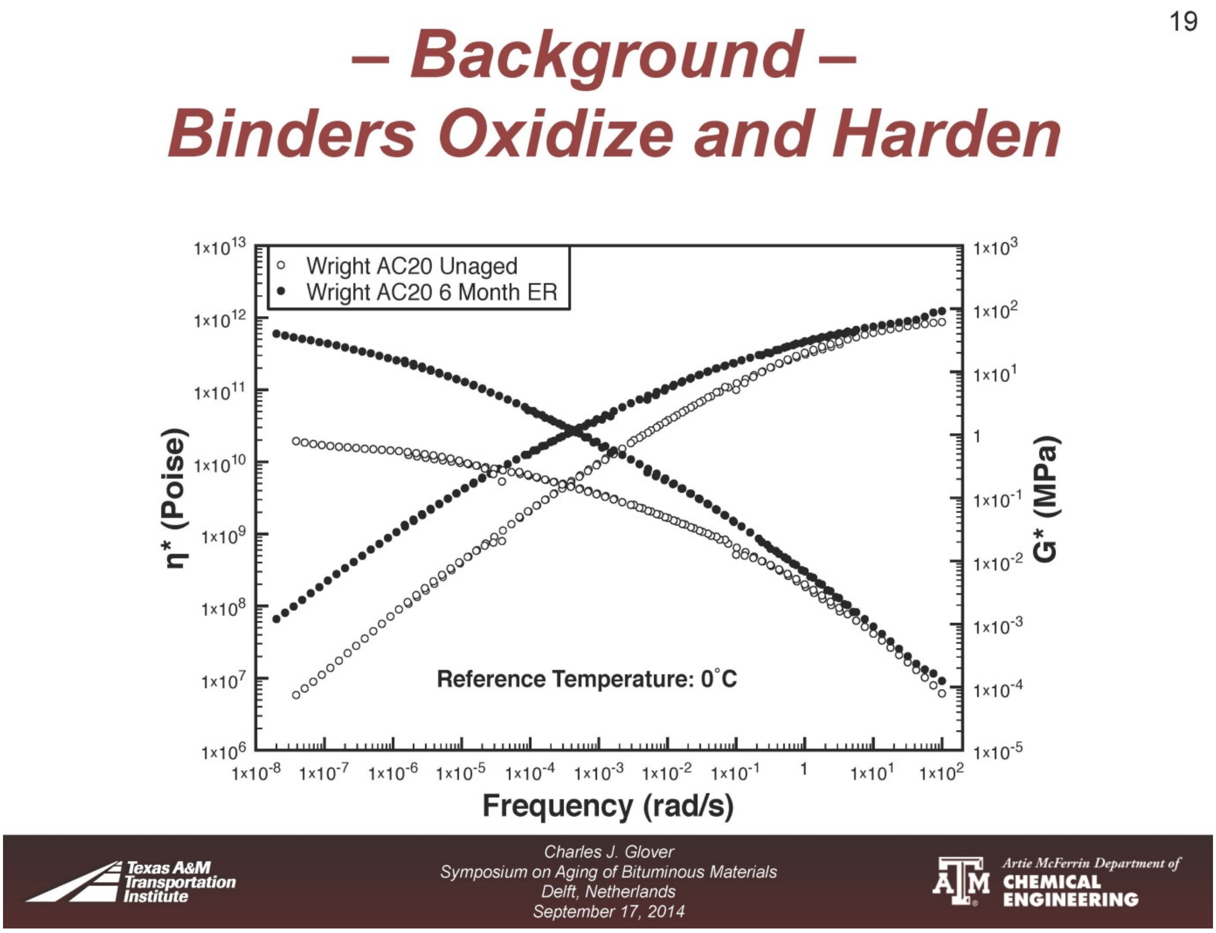
19
– Background –
Binders Oxidize and Harden
Wright AC20 Unaged
Wright AC20 6 Month ER
η* (Poise)
G* (MPa)
Reference Temperature: 0˚C
Frequency (rad/s)
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– Background –
Binder Rheology and Brittleness

*Why DSRFn = G'/(η'/G')?**

G'/(η'/G') = Glover-Rowe parameter
= G*ωcos²δ/sinδ

$$G'/(\eta'/G') = G^{*}\omega\cos^{2}\delta/\sin\delta$$

***at 15 C, 0.005 rad/s**

DSRFn: *Ruan, Y., R.R.Davison, and C.J. Glover, "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003).*

G-R Parameter: *(1) King, G., M. Anderson, D. Hanson, and P. Blankenship: "Using Black Space Diagrams to Predict Age-Induced Cracking," 7th Rilem Intl.Conf on Cracking in Pavements, vol 1, Scarpas, Kringos, Al-Qadi, Loizos (eds.), 2012. (2) R.M. Anderson, G.N. King, D.I. Hanson, P.B. Blankenship, AAPT 80, 615 (2011). (3) Rowe, G.M., Prepared discussion following the Anderson AAPT paper above, AAPT 80, 649-652 (2011).*

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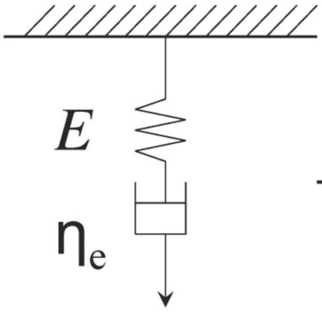
MAXWELL MODEL



$$\frac{L_o}{U_o}\frac{E}{\eta_e}T + \frac{dT}{d\alpha} = \frac{E}{\alpha}$$

$$G' \qquad \frac{\eta'}{G'}, \qquad \frac{G'}{\frac{\eta'}{G'}}$$

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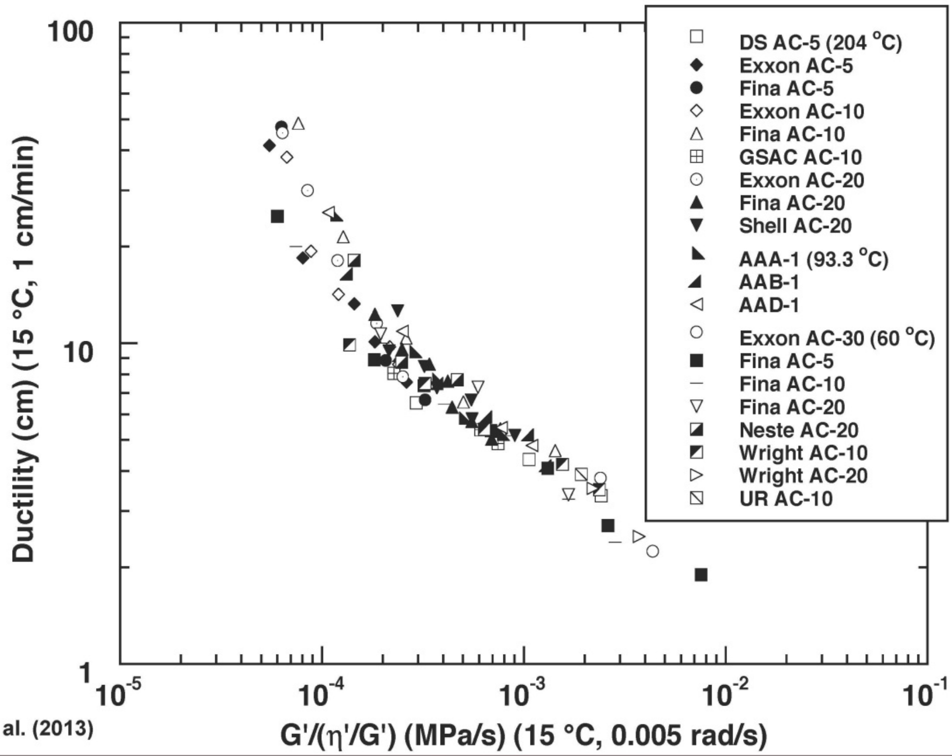
DUCTILITY vs. DSRFn



Ruan et al. (2013)

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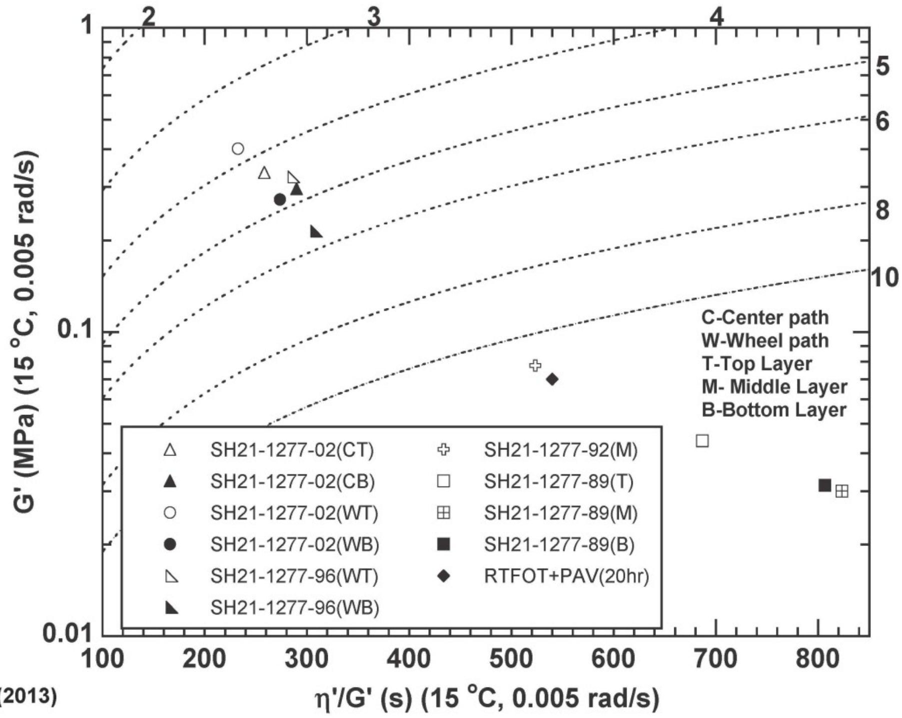
G' vs. η'/G' MAP FOR PAVEMENT MATERIALS



Ruan et al. (2013)

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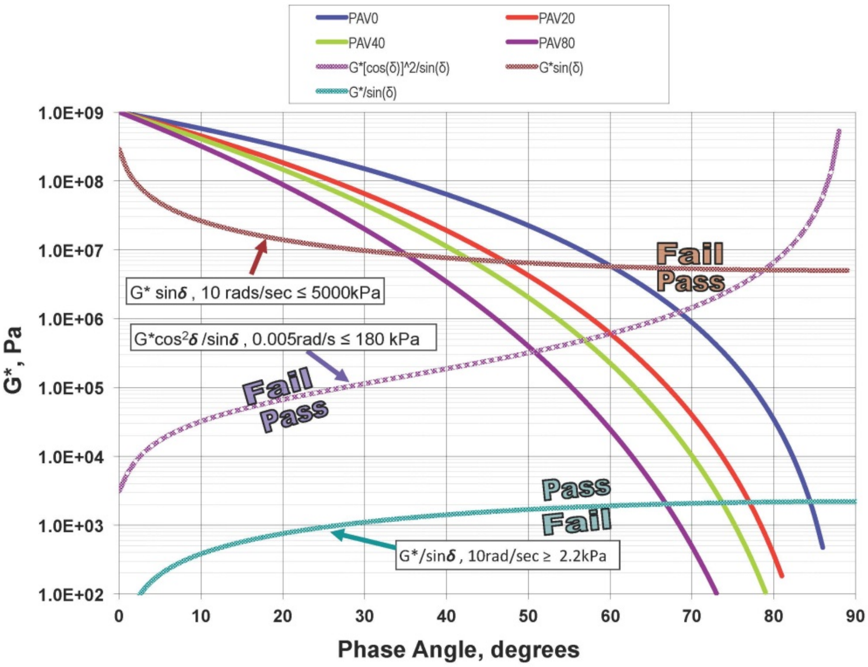
BLACKSPACE MAP FOR PAVEMENT MATERIALS

Rowe, G.M., Prepared discussion following AAPT paper, AAPT 80, 649-652 (2011).

"Glover – Rowe" parameter named by Gayle King: see slide 20.



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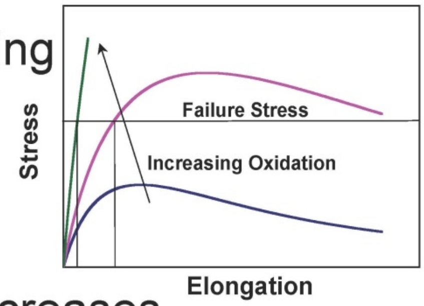
BINDER RHEOLOGY AND BRITTLENESS - DSRFn

- Binders harden with oxidative aging
  - G', η' increase; δ decreases
  - Stresses build faster and relax slower under deformation
  - Consequently, failure strain decreases
- Binders march across the DSR map with increased oxidative aging ("march to death")
- DSR Function characterizes stress building (elastic spring) versus stress relief (viscous flow)



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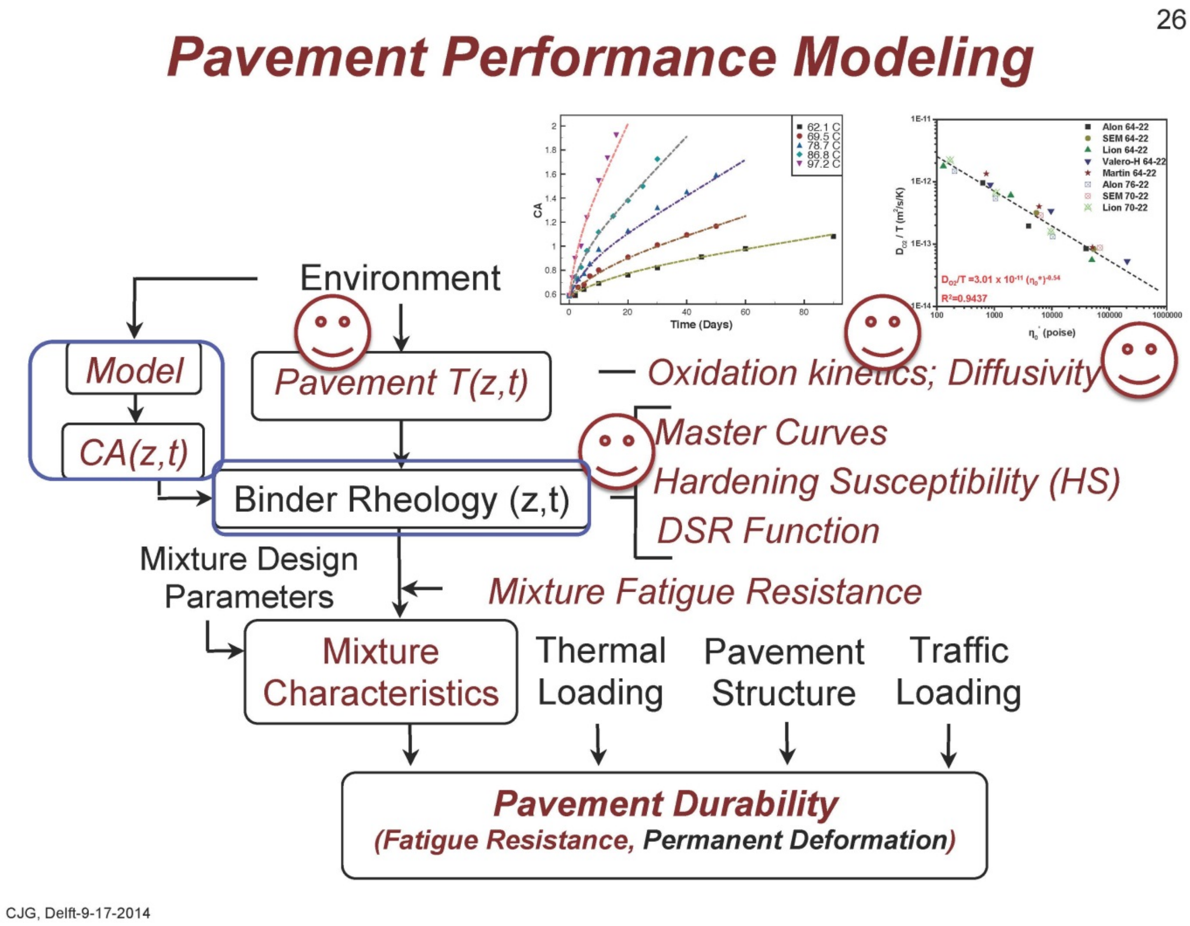
26
Pavement Performance Modeling
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Master Curves
Hardening Susceptibility (HS)
DSR Function
Binder Rheology (z,t)
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
Time (Days)
CA
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
R²=0.9437
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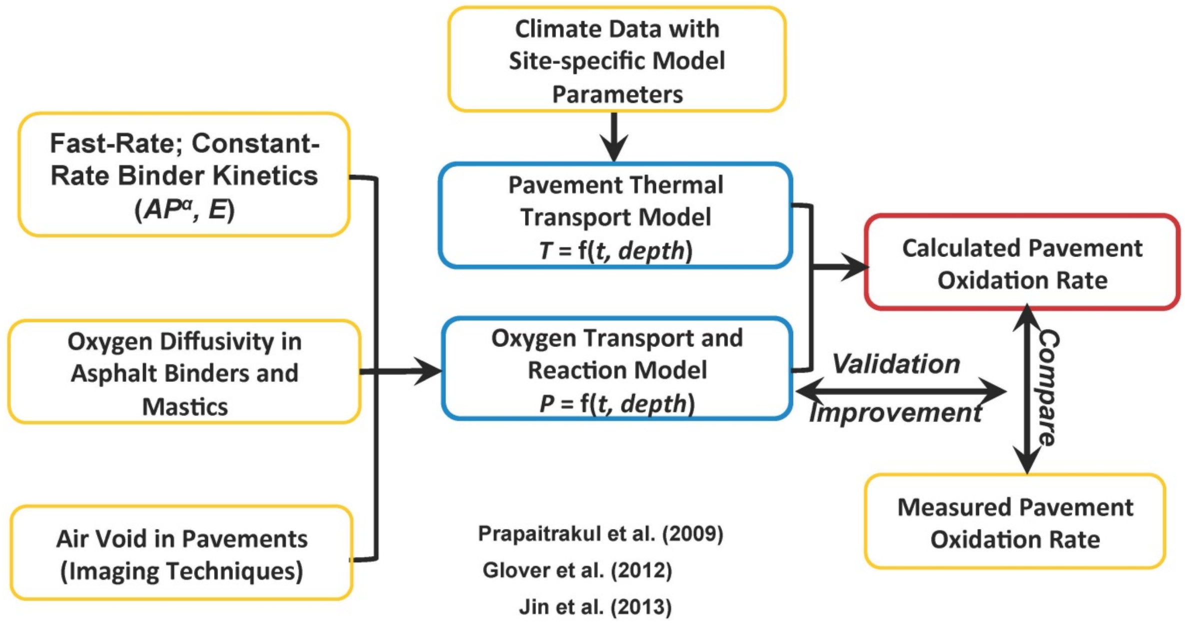
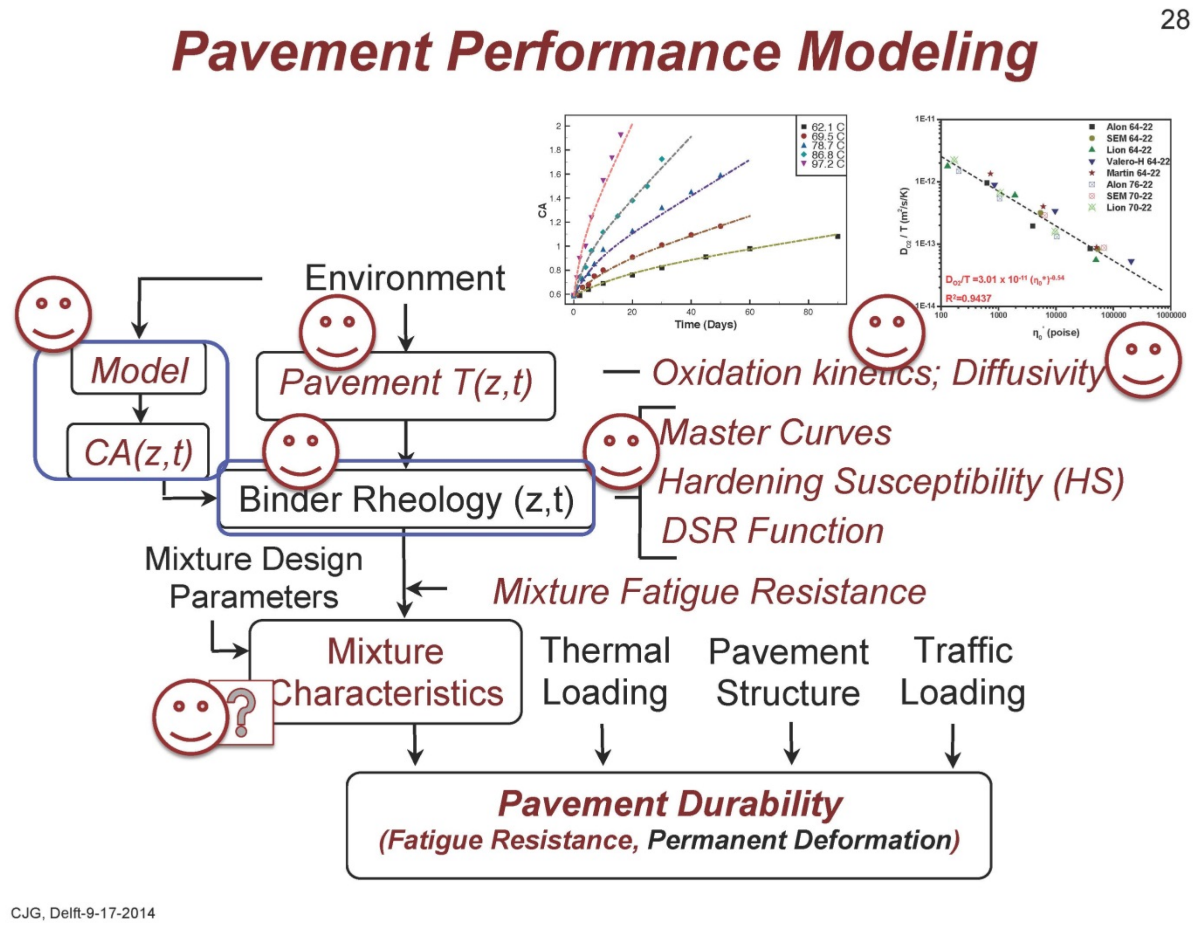
Background: Pavement Oxidation Model




28
Pavement Performance Modeling
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Master Curves
Hardening Susceptibility (HS)
DSR Function
Binder Rheology (z,t)
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
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So, the Design Procedure (and Aging test) is:

- Using ***original*** binder:
  - Kinetics measurements: POV (3 mos)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calcs of temp history and profile
  - Model calcs of CA growth and hardening
  - Mixture response to hardening
- But, with no original binder, all is lost, right? **NO!**

30

And the Forensics Procedure (on an interesting aged pavement) is:

- Using ***extracted and recovered*** binder:
  - Kinetics measurements: POV (3 mos)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calcs of temp history and profile
  - Model calcs of CA growth and hardening
  - Mixture response to hardening
- But **what about the POV 3 mos procedure**?

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Oxidation Kinetics Problem: It Takes Time to Determine the Parameters – 3 months!
Oxidation Kinetics Solution (?): Measurements in the PAV

- Accelerate aging with higher air pressure
- **Big Question**: Are the kinetics at 1 atm air comparable to kinetics at 20 atm air?

van Oort, *Durability of Asphalt, 1956*
Herrington, P.R. *Petroleum Science and Technology, Vol.16, 1998*

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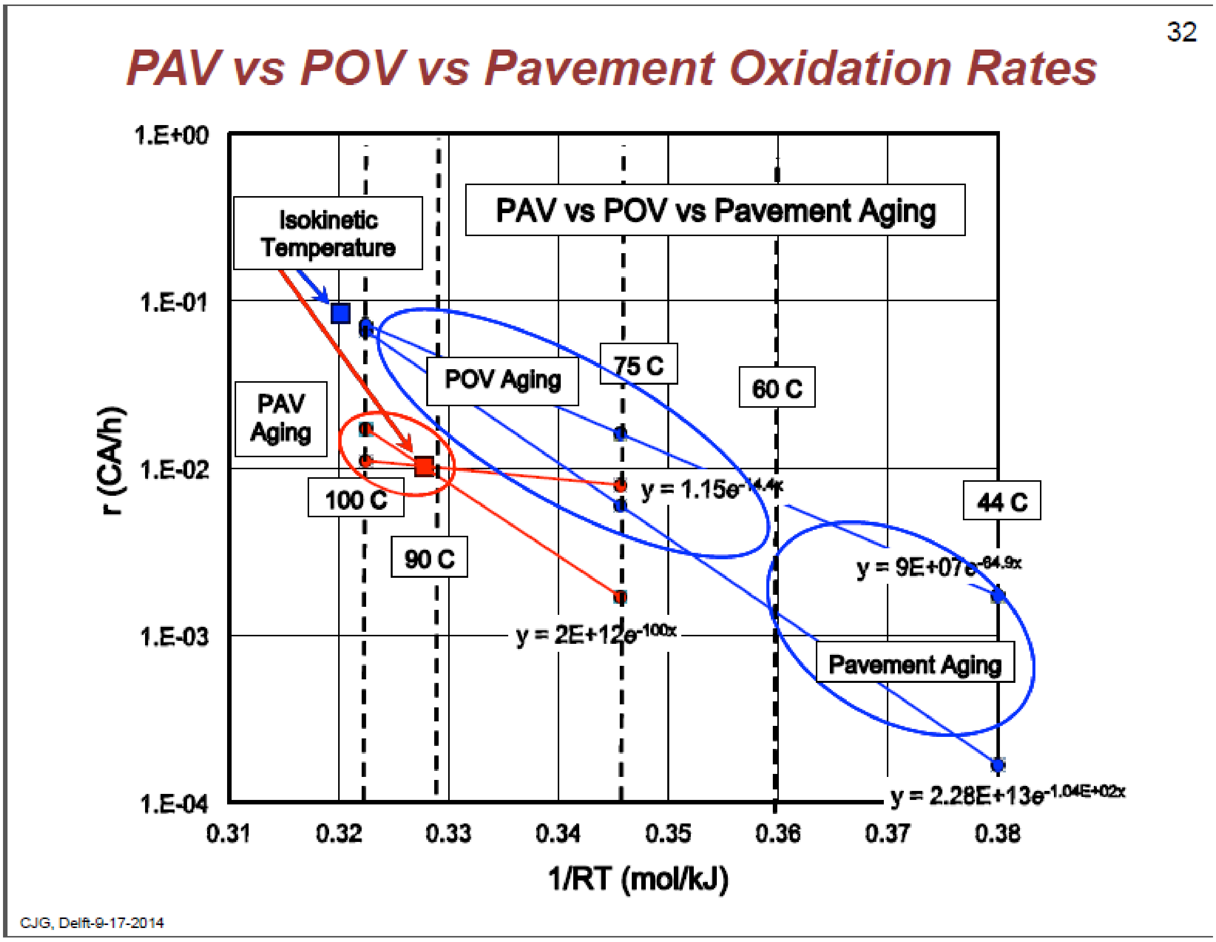
32
PAV vs POV vs Pavement Oxidation Rates
Isokinetic Temperature
PAV vs POV vs Pavement Aging
POV Aging
75 C
60 C
PAV Aging
100 C
90 C
44 C
y = 1.15e-14.4x
y = 9E+07e-84.9x
y = 2E+12e-100x
Pavement Aging
y = 2.28E+13e-1.04E+02x
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
r (CA/h)
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
1/RT (mol/kJ)
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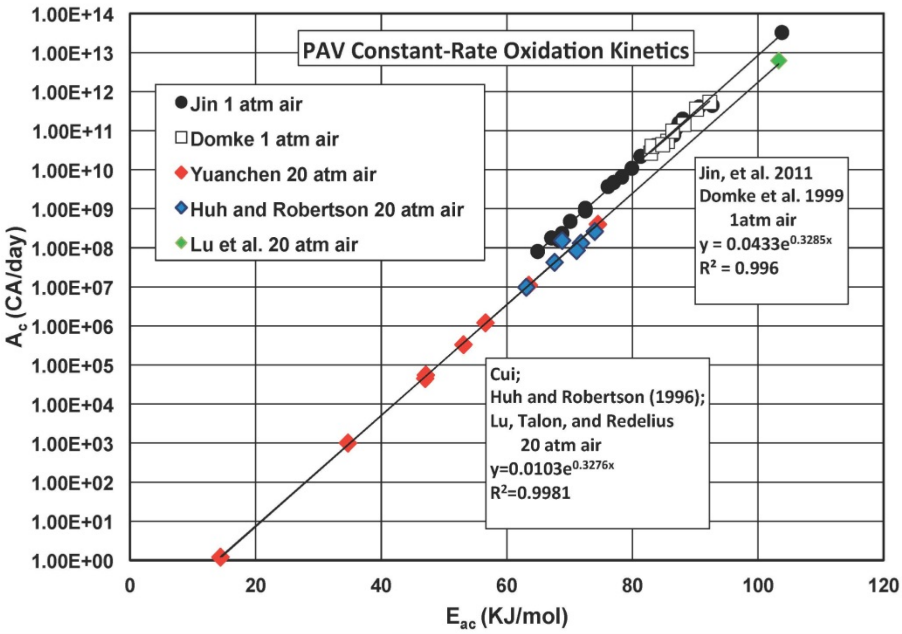
PAV Ac versus Eac Correlation



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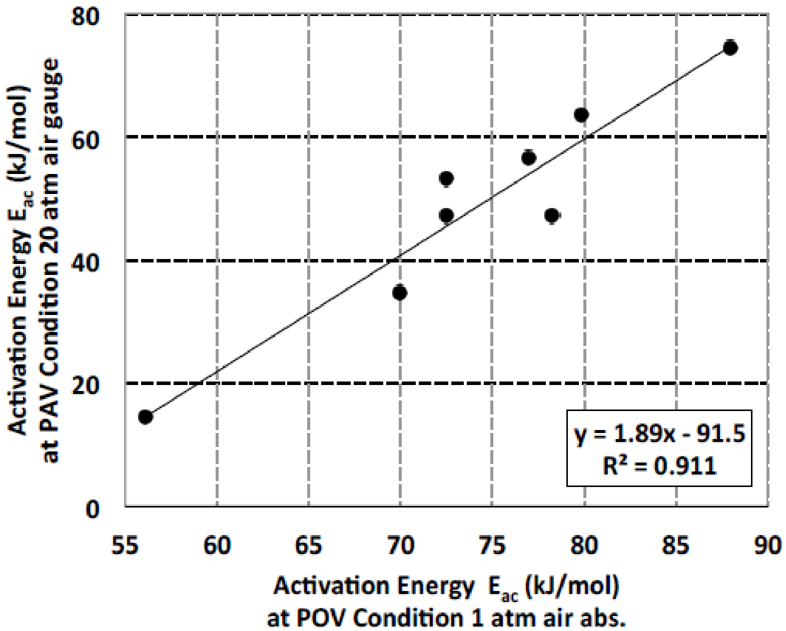
PAV vs POV Activation Energies



Cui et al. (2014)

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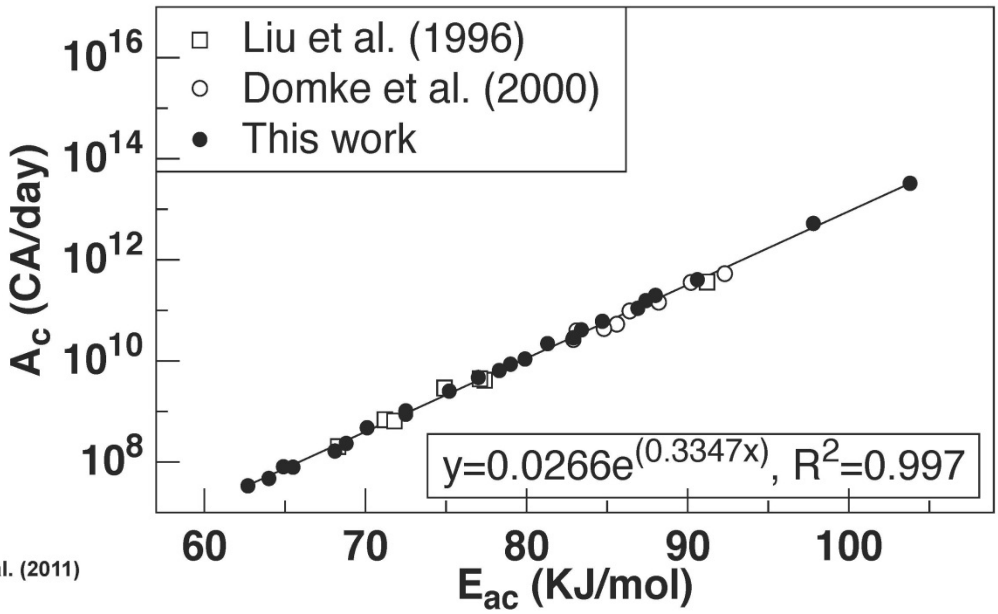
Overview: Kinetics Correlations



Jin et al. (2011)

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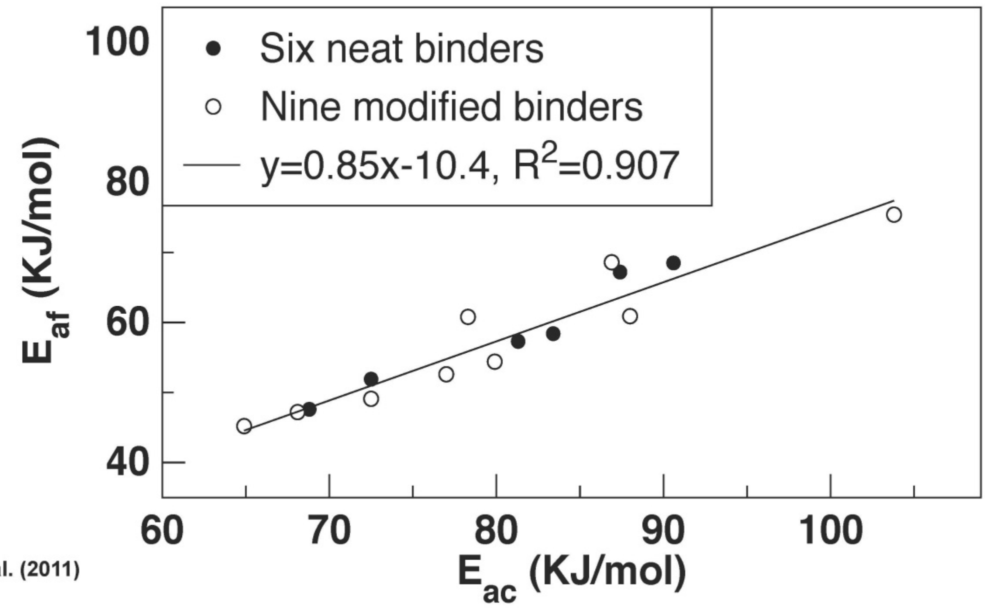
Overview: Kinetics Correlations



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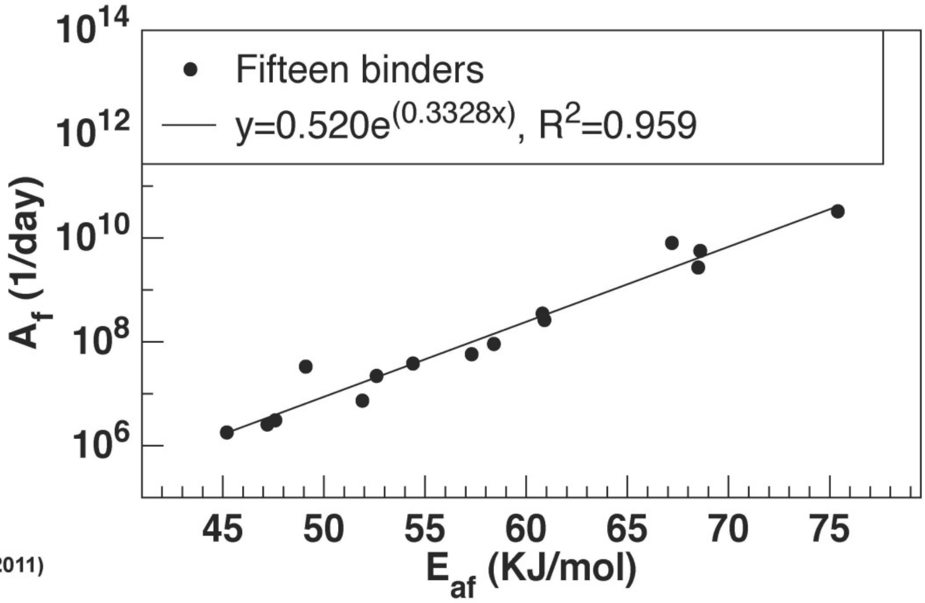
Overview: Kinetics Correlations



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So: A strategy to estimate 1 atm kinetics parameters from PAV!

- Measure E_{ac}, A_c in PAV; verify their fit to the existing correlation (data consistency check)
- Using E_{ac} (1 atm) vs E_{ac} (20 atm), determine 1 atm E_{ac}
- Using 1 atm correlations, use E_{ac} to determine other parameters at 1 atm: A_c, E_{af}, A_f
- Determine M separately from 1 atm data
- Time: approximately 1 week!

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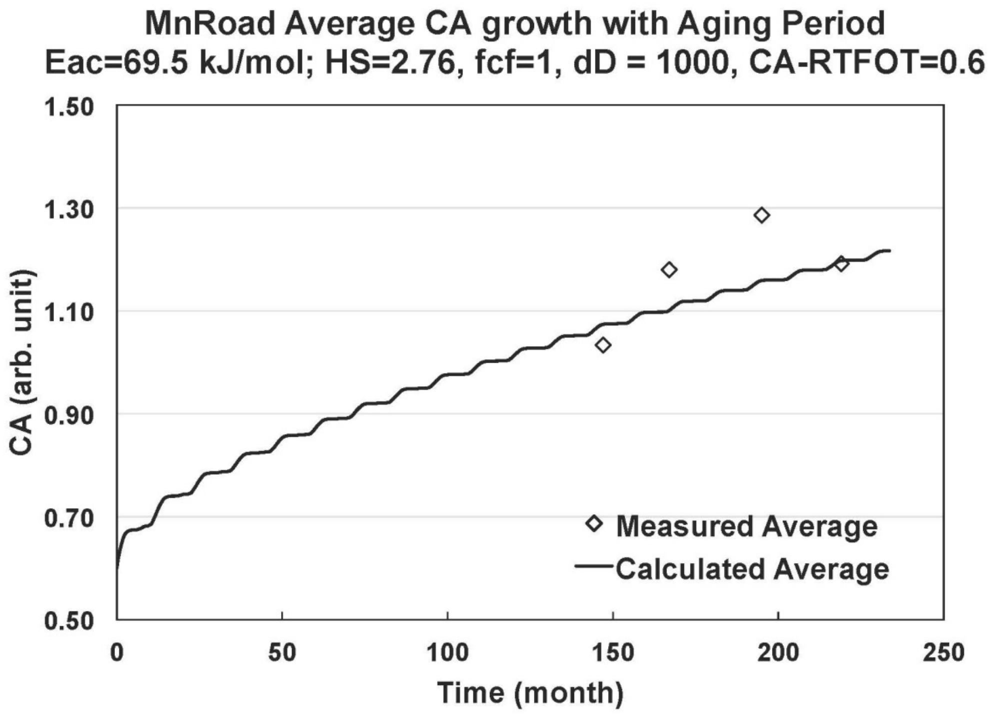
So, the Forensics Procedure (on an interesting pavement) is:

- Using ***extracted and recovered*** binder:
  - Kinetics measurements: PAV (1 week)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calculations of temp history and profile
  - Model calculations of CA growth and hardening
  - Mixture response to hardening

40

Example Oxidation Modeling - MnRoad Cell 1 -



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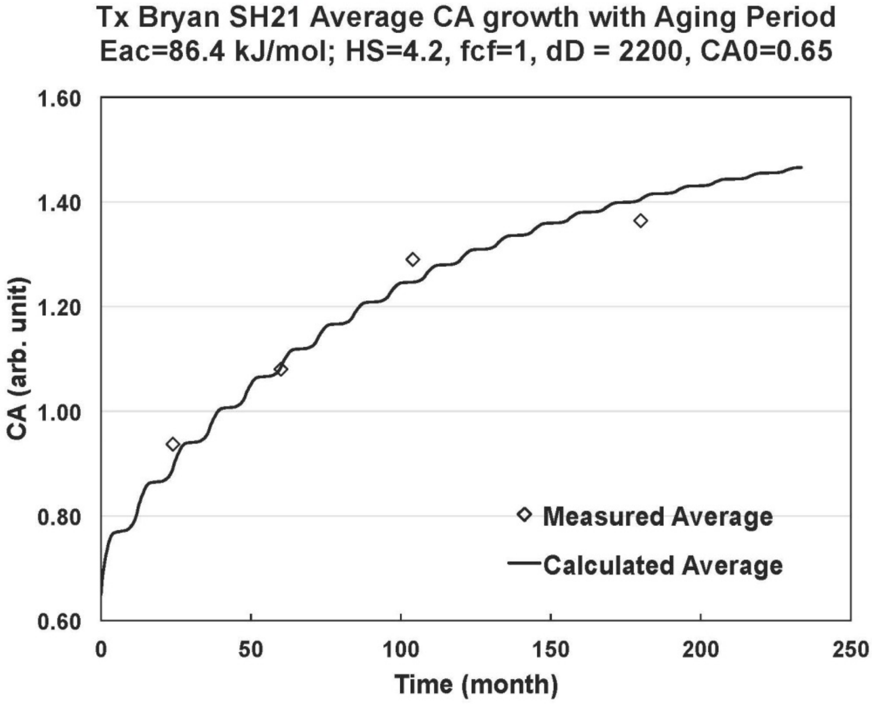
Example Oxidation Modeling - Bryan, Tx SH 21 -



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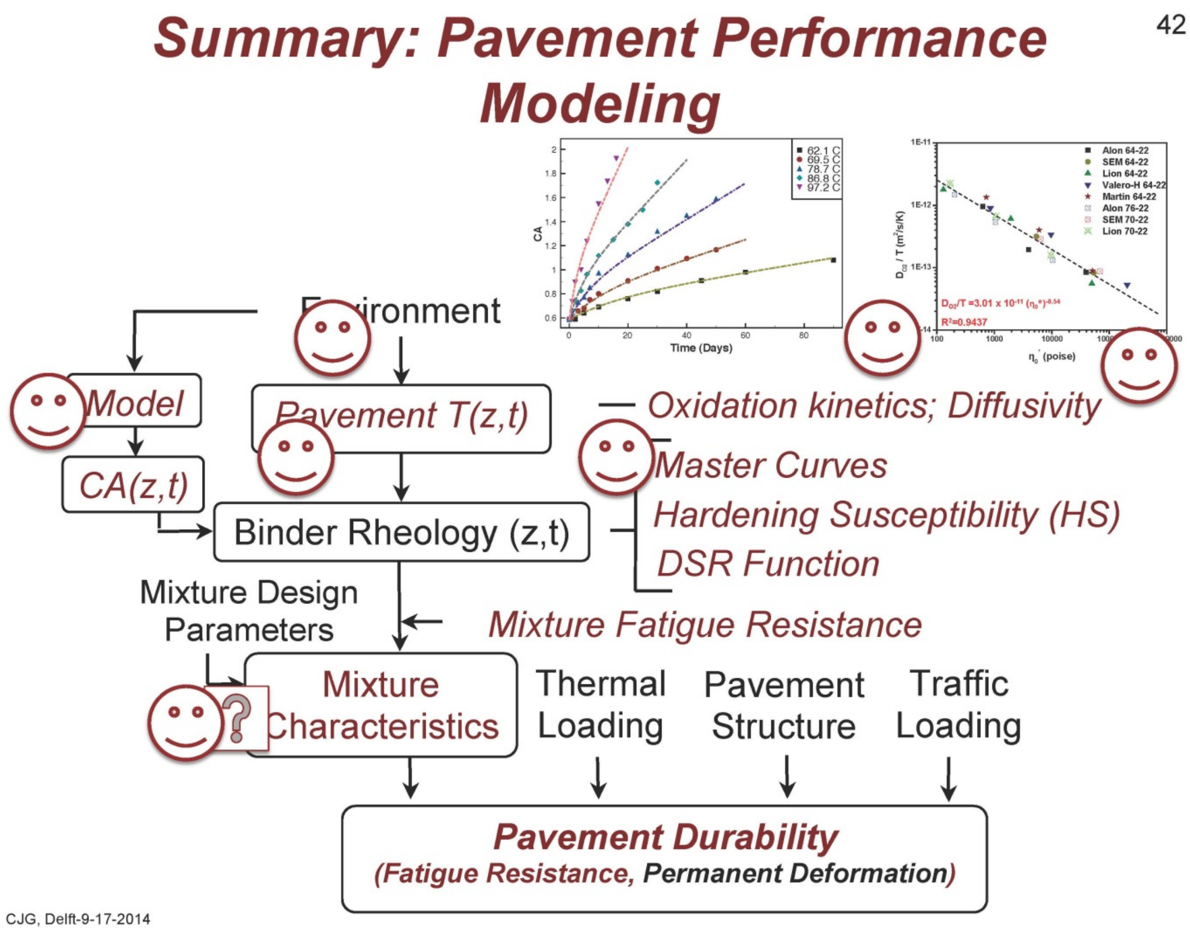

Conclusions

- Pavement binders ***oxidize and harden over time***
  - A ***relentless*** process
  - Occurs ***well below the pavement surface***
  - Hardening results in ***binder embrittlement***: fracture at a lower strain; "March to Death"
- ***Long-term goal has been to understand this process*** quantitatively and its impact on pavement durability
- These ***fundamentals can be used for***:
  - ***design*** that is specific to pavement site
  - ***forensics*** studies of in-service pavements
  - ***fast oxidative aging test of binders***, specific to each pavement site

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Thank You!

- TxDOT for multiple projects over many years leading up to and including pavement oxidation modeling and binder kinetics
- The FHWA and the Asphalt Research Consortium for support of elements of the pavement model
- Tom Scarpas and Sandra Erkens for the invitation to this symposium

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- Prapaitrakul N., Jin X., Han R., and Glover, C. J. "A Transport Model of Asphalt Binder Oxidation in Pavements," Road Materials and Pavement Design, 10 (Special Issue), 95-113 (2009).
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- Ruan, Y., Davison, R.R., and Glover, C.J., "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003).

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8.2 Ron Glaser, WRI, Advances in asphalt binder oxidation understanding with practical implications: Chemical and rheological behavior.

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Oxidation, Rheology, and Durability

Ron Glaser
Fred Turner
J.P Planche
Western Research Institute
Laramie, Wyoming
USA

TU Delft 2014

Western Research INSTITUTE

Oxidation, Rheology, and Durability

An overview of the primary effects of oxidation on pavements

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Oxidation, Rheology, and Durability

- **Oxidation gradients form in pavements**
- **Extreme stiffness gradients are the result**

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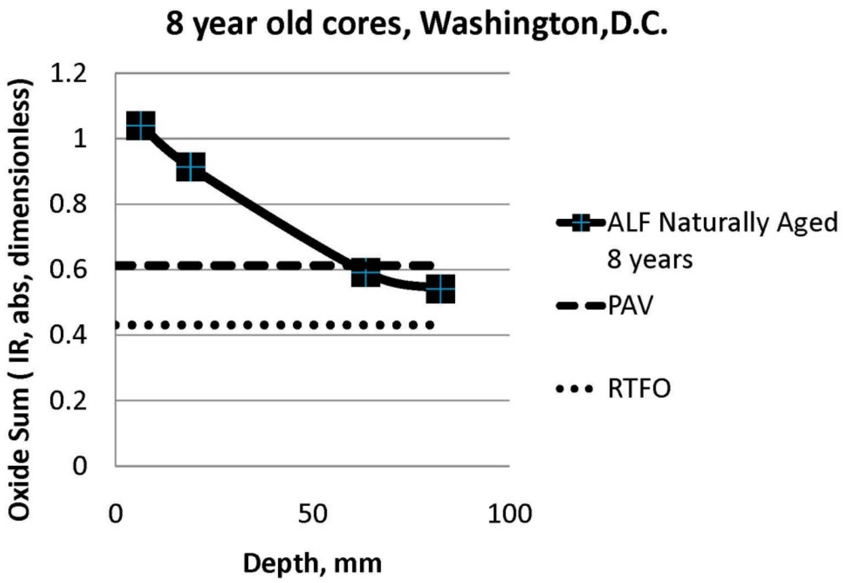
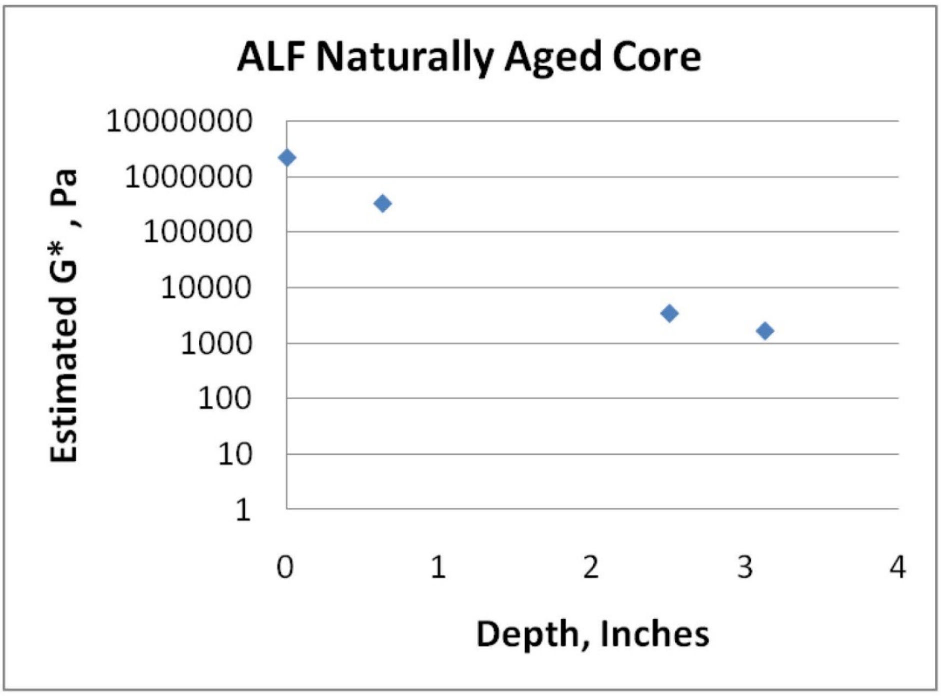
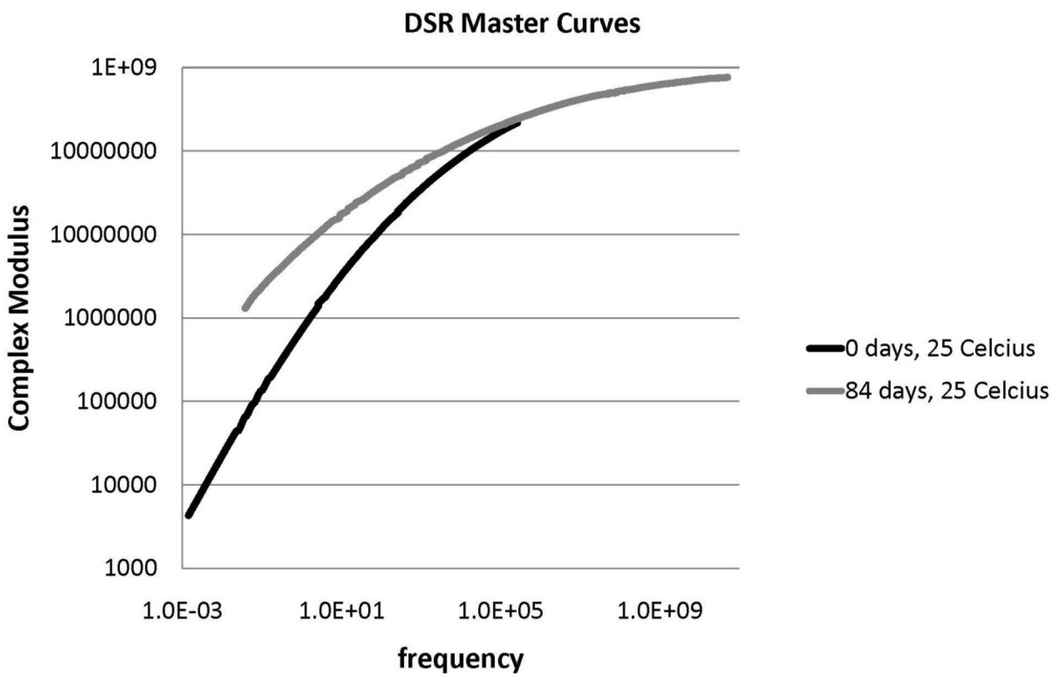
Oxidation in Pavements



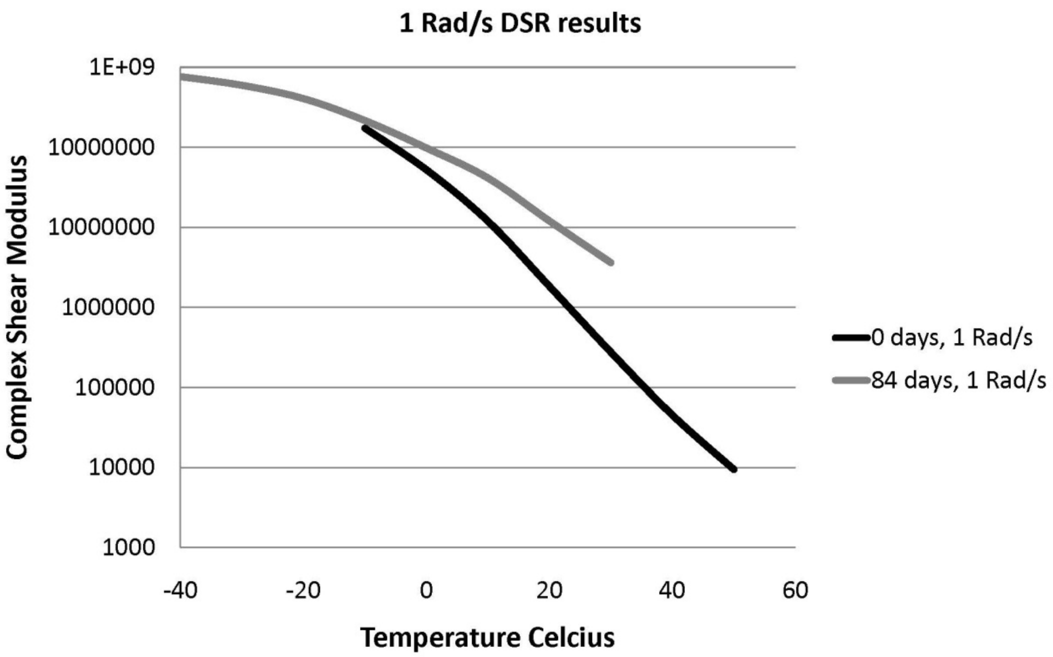
Complex Modulus with Depth



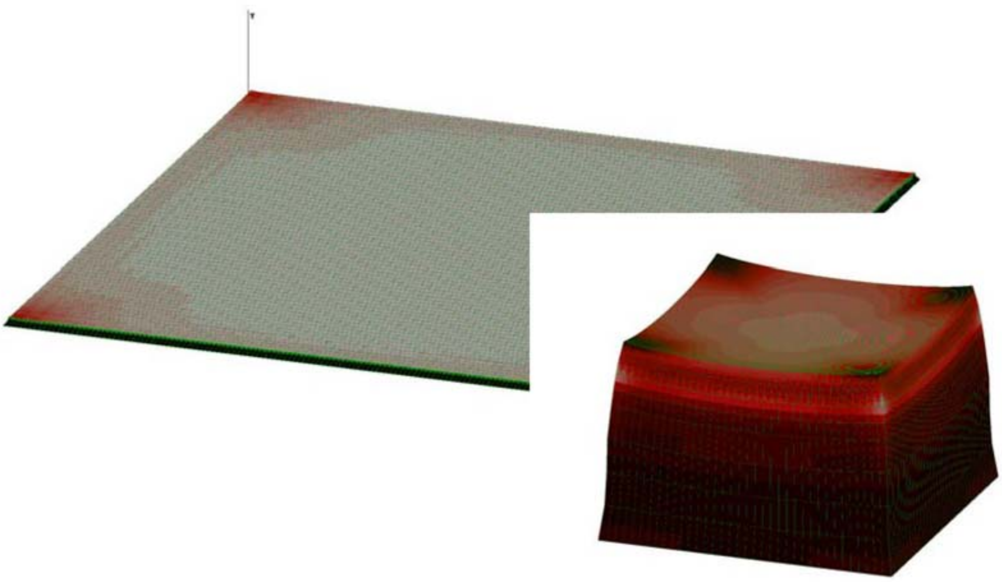
Master Curve changes with oxidation



Master Curve changes with oxidation



Static-Elastic Modeling of Thermal Stresses… Aging and Block Cracking



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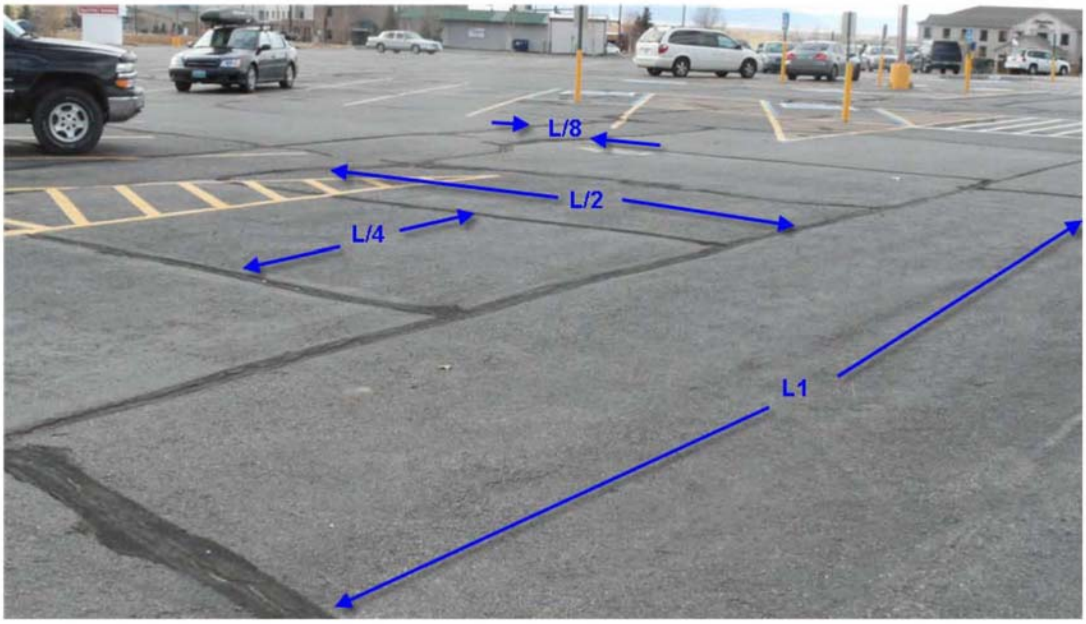
Static-Elastic Modeling of Thermal Stresses… Aging and Block Cracking



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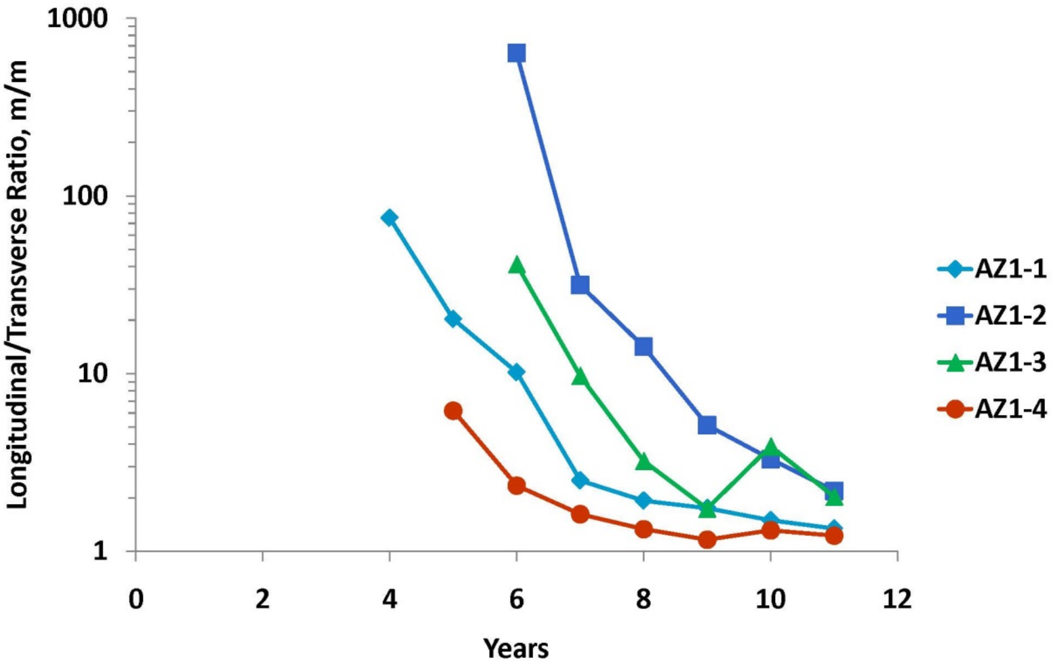
AZ1 Distress Data



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Pavement Performance Prediction

- Knowing this gradient, mechanical deflection and fracture models for pavement can predict it's performance

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Why Gradients

- The rate of oxidation at any point in the pavement depends on temperature and oxygen concentration.
- Daily temperature extremes are greatest at the surface, so rates are fastest at the surface.
- Access to oxygen is greatest at the surface as well.

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Can we predict the stiffness gradient?

- The physics of heat transfer are well known. Very good transient temperature models exist.
- The physics of mass transfer (diffusion, permeation, capillary flow, thermal pumping) are also well known.
- These must be coupled with the oxygen consumption to predict the concentration of oxygen in each point in the pavement section.
- The chemistry of asphalt oxidation(oxygen consumption) is less well known, but is understood well enough get a rate calculation
- The relationship between mechanical properties (rheology) and oxidation must also be understood.

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Fundamental Approach Oxidation Rate

- "Fast and Slow Reaction" Dual Reaction Mechanism (Petersen) rate limiting steps

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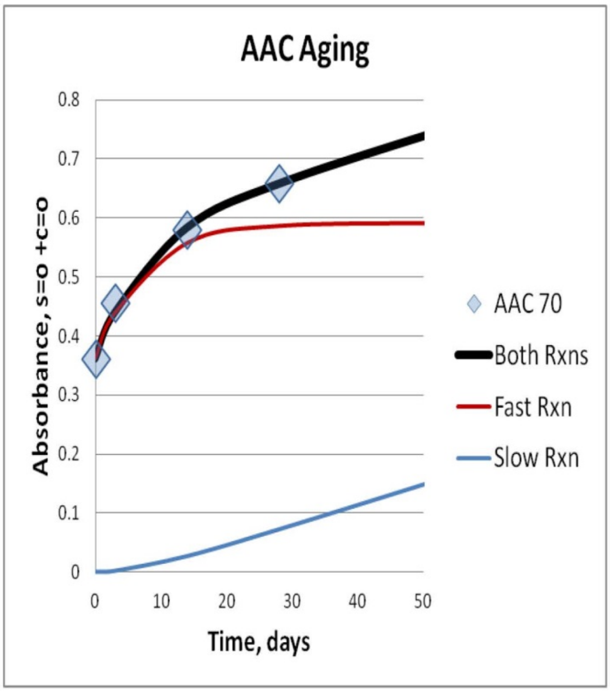
Dual Reaction Model



Fast Reaction:

RM+O_2→Products +FR*

Slow Reaction:

BC+FR*→BC*+O_2→Products +FR*

RM is reactive material

O_2 is molecular oxygen

FR* generic free radical

BC is benzyl carbon

BC* is benzyl carbon radical

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Universal Rate Equation ?

$$\left[P(t)\right] = M\left(1-\frac{k_2}{k_1}\right)(1-e^{-k_1 t}) + k_2 M t + \left[P_{1,0}\right]$$

$$[sulfoxide + carbonyl] =$$

$$M\left(1-\frac{k_2}{k_1}\right)(1-e^{-k_1 {P_{O_2}}^{n} t}) + k_2 {P_{O_2}}^{m} M t$$

$$+\left[sulfoxide + carbonyl\right]_{rtfo}$$

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One Adjustable parameter

- 34 binders fit with fit qualities exceeding 0.9 (r-squared)
- Also works with RAP-Virgin Binder Blends using simple volumetric blending rules
- Also works with PMA

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Complete Picture

- Chemical rate information alone is useless to the pavement designer
- We also need the relationship to rheology
- Empirical data fits suggest a log-linear relationship exists between asphalt binders and rheological master curves
- These relationships depend upon the source, but only two oxidation condition samples are needed to find the relationship. If pressure acceleration is used, a four sample matrix is required.

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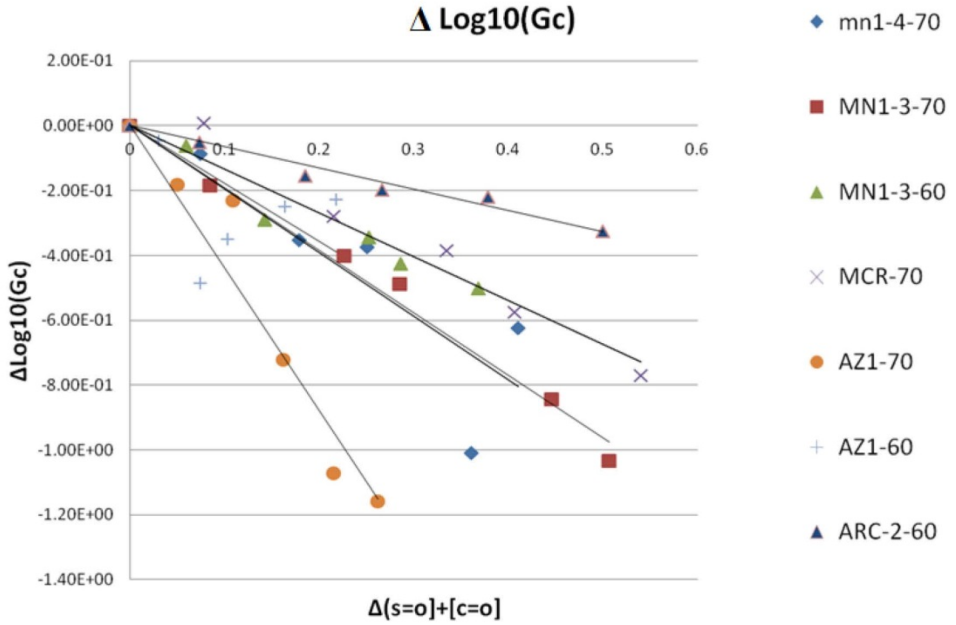
Example rheology correlations



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Moving Forward

- **Long oxidation tests are not practical for routine characterization**
- **A good deal of our work focuses on this issue, developing practical tests for specification and mechanical model inputs.**
- **We also look carefully at detailed chemistry for material design solutions/opportunites**

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Accelerate the reaction

- The reactive material can be found from the y intercept and slope with a bit of algebra from the long term data.
- But, we need to do the test quickly
- Pressurized Differential Scanning Calorimetry (PDSC) is being studied to investigate acceleration options.
- We have found the mechanism is more complex at elevated temperature and pressure
- We have a preliminary model that fits the available data
- Once validated (and perhaps improved) , the rate expression for a binder could be determined in a day, not 2 months.
- We are also looking at direct chemical methods to eliminate oxidation tests and rheology altogether.

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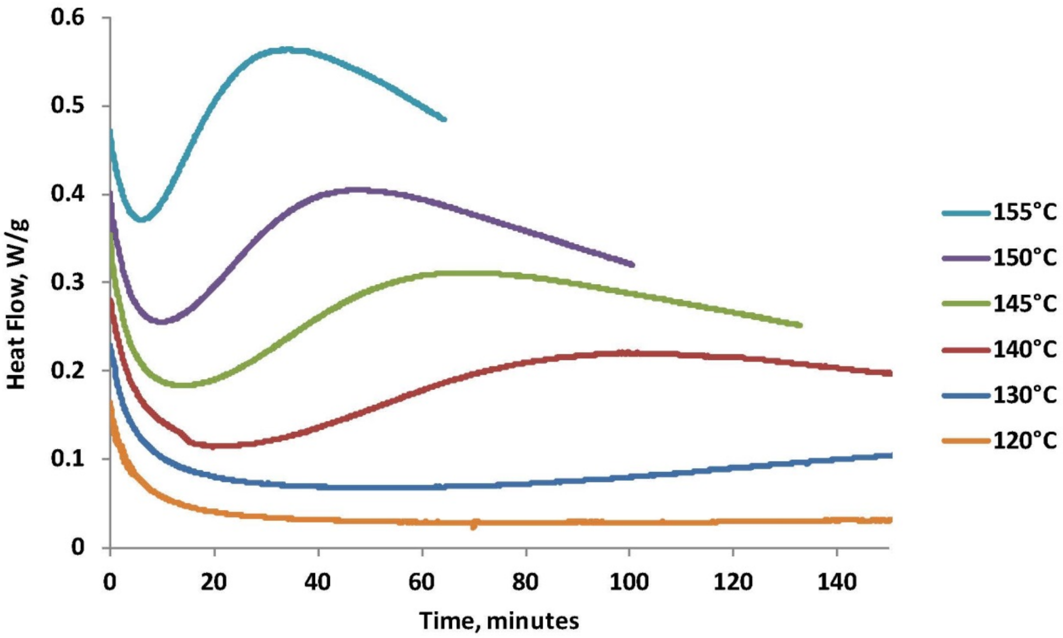
Heat flow overlay at 550 psia O_2



2

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Extended Model

$$M + O_2 \xrightarrow{k_1} P_1 + F_1 ; P_1 \xrightarrow{k4} F_3$$

$$F_1 + C_3 \xrightarrow{fast} C_3^* + O_2 \xrightarrow{k_2} F_1 + nF_2 + P_2$$

$$F_2 + F_3 \xrightarrow{k_3} \xrightarrow{fast\ oxidation\ steps} P_3$$

- F_1 is small and mobile
- F_2 and F_3 are big and have some steric hindrance
- k_3 should be independent of pressure

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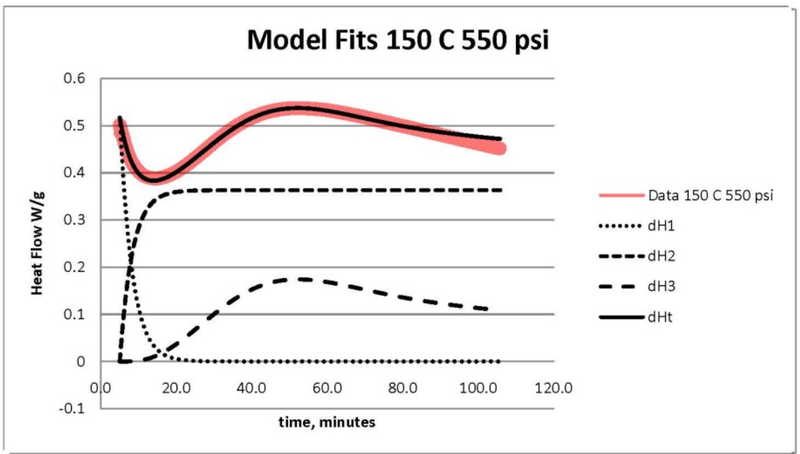
Fits



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Direct chemical methods

- IR
- SAR-AD
- GPC (SEC)

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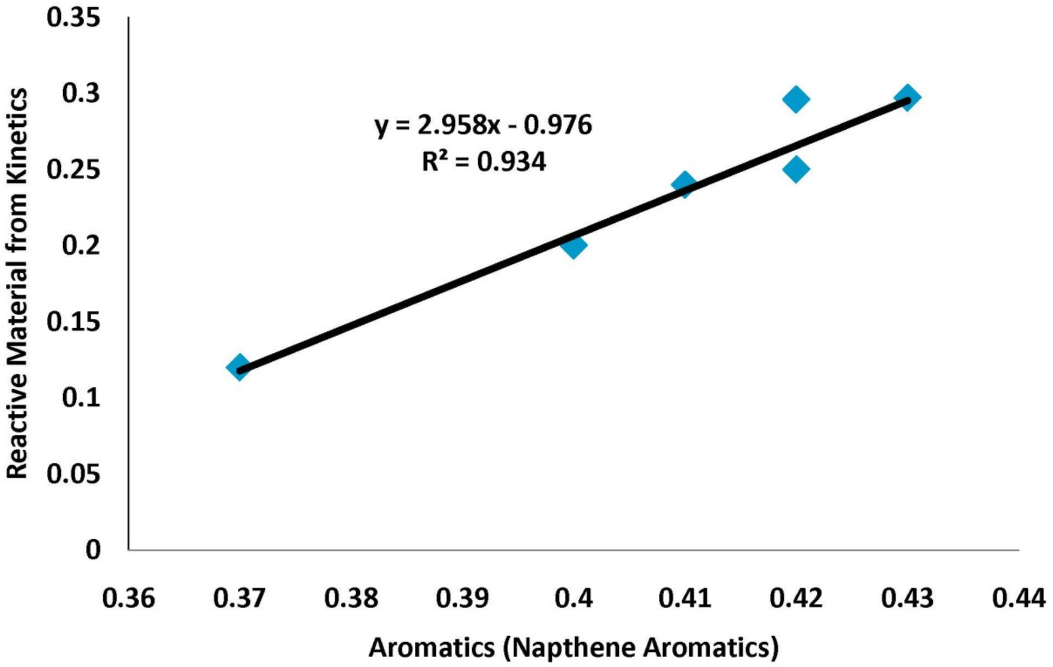
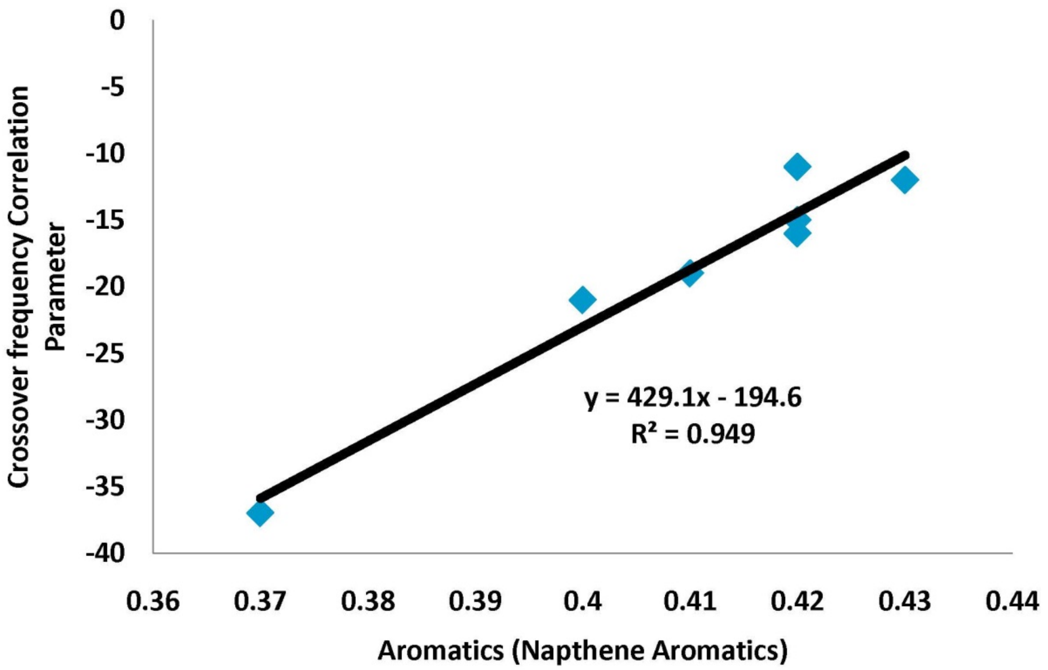
- Best results for directly obtaining reactive material and the rheology response has been from SARA data

RTFO SARA & Reactive Material



RTFO SARA and Crossover Frequency Correlation Parameter



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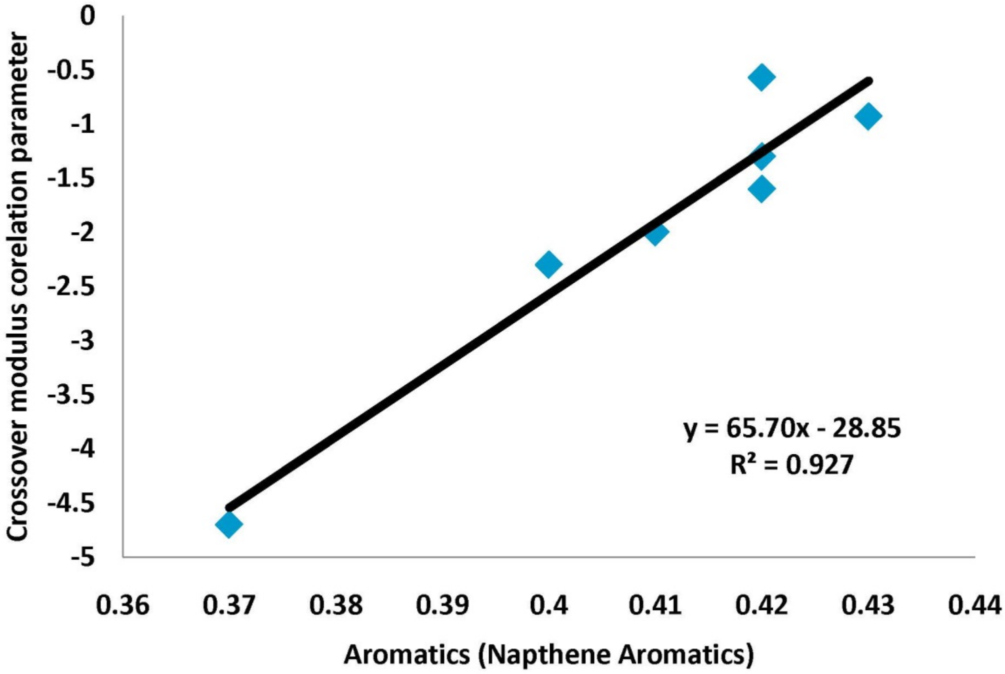
RTFO SARA and Crossover Modulus Correlation Parameter



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Near Term Approaches

- **Generated samples from PAV and extended PAV at 2 pressures can be analyzed with IR and DSR to get the reaction rate and rheological behavior.**
- **This approach would take about a week, perhaps a little less.**

Conclusions

- **Much better oxidation characterization information suitable for specification and/or model predictions can be obtained with some minor modifications to accepted methods (will need to be validated).**
- **Very rapid methods are on the horizon and appear to be feasible.**

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8.3 Hilde Soenen, Nynas, What happens during aging and where is aging happening?

What happens during aging and where is aging happening?

Hilde Soenen

Symposium Delft – 17-09-2014

Outline | Accelarated aging | Field aging studies | Binder films

Outline

- **PART 1:** Accelarated aging in RTFOT+PAV:
  - -Rheological and chemical changes during standard accelarated aging tests
  - -How important is the aging temperature ?
- **PART 2:** Field aging, using recovered binders
  - -Unmodified (& pmbs)
- **PART 3:** Field aging, leaving a bitumen film outside
  - -To avoid the recovery step, bitumen films were left outside

2

PART I: Accelarated aging

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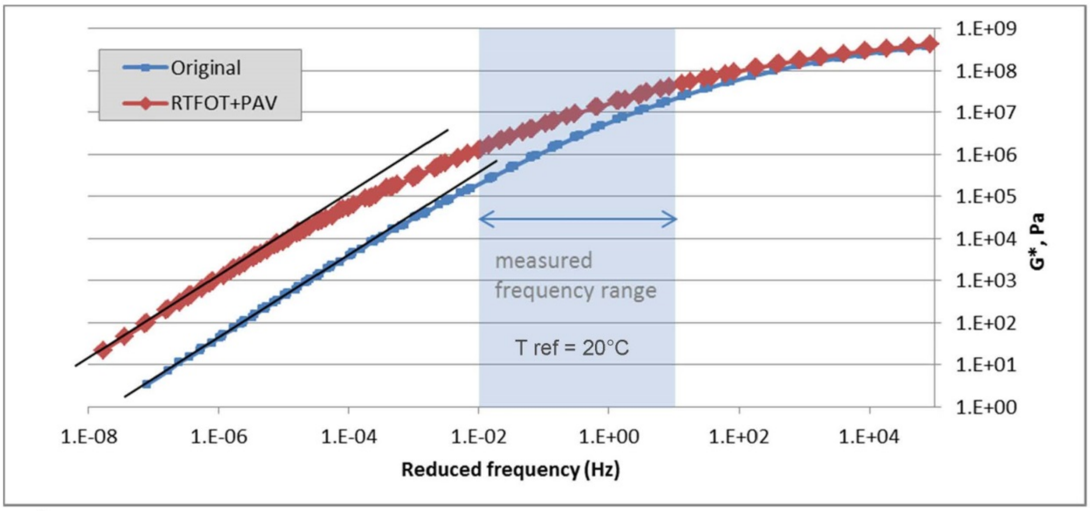
		Pen	R&B	PI	melting enthalpy (J/g)
B1	SR + oxidation	5	104.5	2.57	0.0
B2	solvent deasphalted	5	74.2	-0.74	0.0
B3		12	65	-0.86	1.4
B4	VB	15	64.2	-0.64	5.6
B5		15	62.6	-0.90	2.1
B6	SR	20	62.2	-0.49	0.0
B7	SR + air rectified	25	61.5	-0.21	0.0
B8	Blend: solvent deasphalted + B160/220	27	55.5	-1.22	2.7
B9		27	61.5	-0.06	3.5
B10	VB	38	54.3	-0.80	5.4
B11		42	51.3	-1.27	2.8
B12		51	49.1	-1.39	6.0
B13	VB	52	49	-1.37	6.8
B14	VB + air rectified	52	49.8	-1.17	6.2
B15		53	49.9	-1.10	5.0
B16		61	47.7	-1.34	4.9
B17		62	50	-0.69	6.3
B18	SR	64	47.7	-1.23	0.0
B19	VB	67	46.8	-1.36	7.6
B20		70	46.1	-1.46	3.8
B21	VB	80	45.8	-1.20	7.1
B22		81	45.5	-1.25	2.4
B23		107	43.5	-1.09	4.0
B24	VB	187	38.5	-1.03	5.4
B25	SR	187	36.9	-1.80	0.0
B26	VB	190	39.2	-0.63	9.6
B27		200	37.7	-1.11	6.1

VB: Visbroken
SR: Straight-run or distilled

3

Accelarated aging

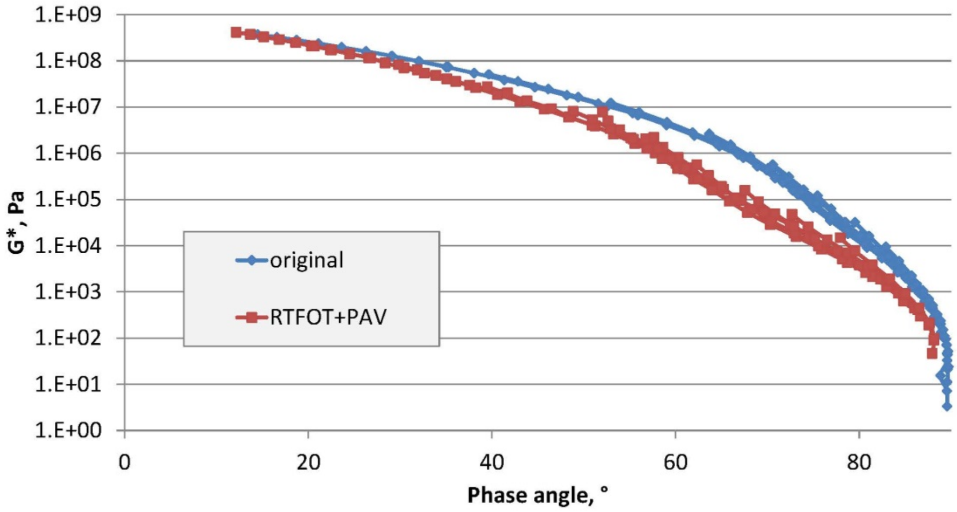
1. Mechanical changes in the linear visco-elastic region:



4

Accelarated aging

1. Mechanical changes in the linear visco-elastic region:



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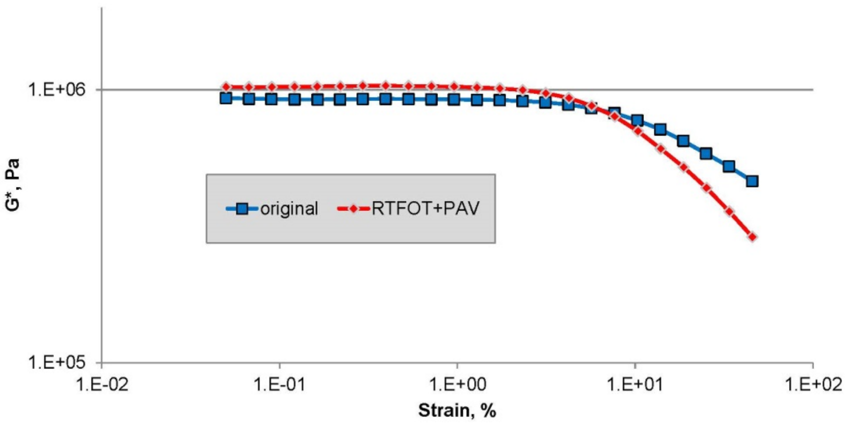
Accelarated aging

2. Mechanical changes in the non-linear visco-elastic region:



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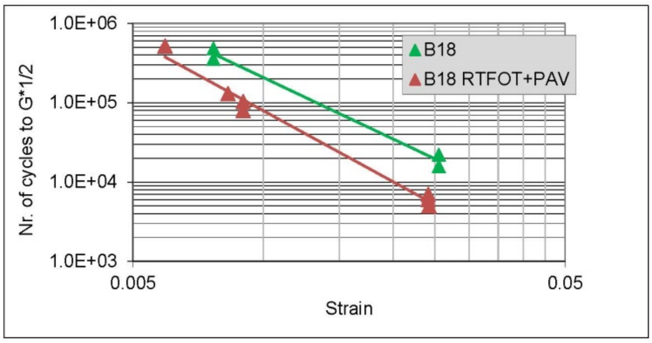
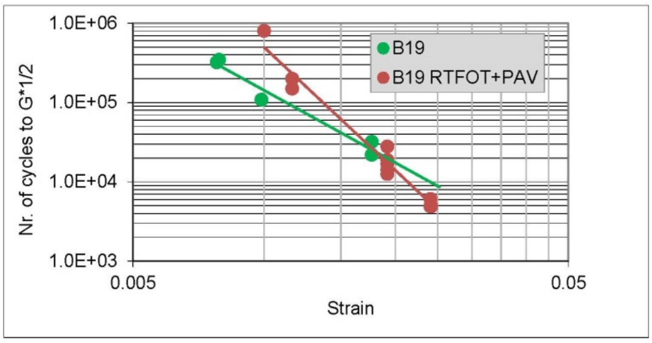
Accelarated aging

3. Mechanical changes in the fatigue behavior:

(Controlled strain test in DSR, 10°C, 10Hz)



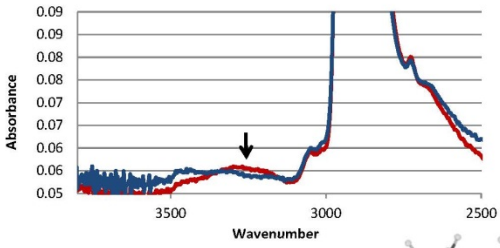


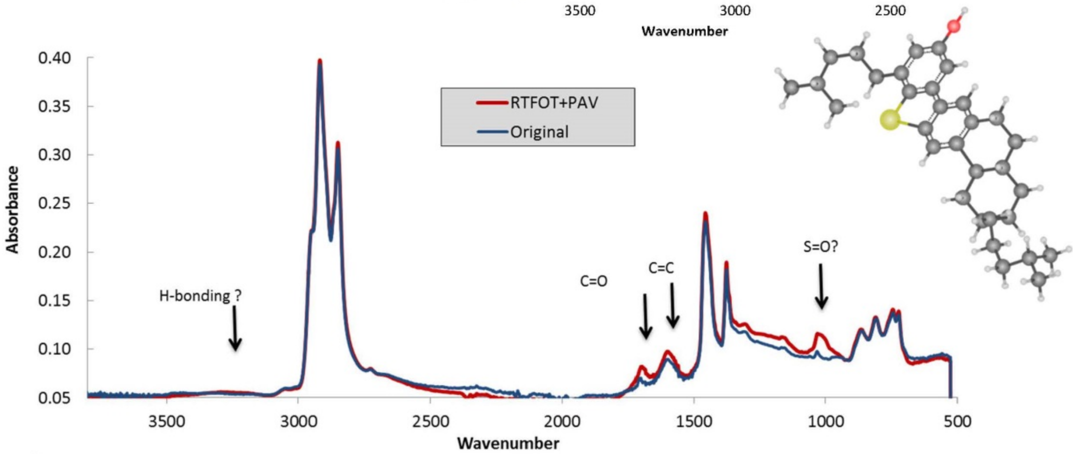
Upper figure: SR
Lower figure: VB

7

Accelarated aging

4. Chemical changes, FT-IR:





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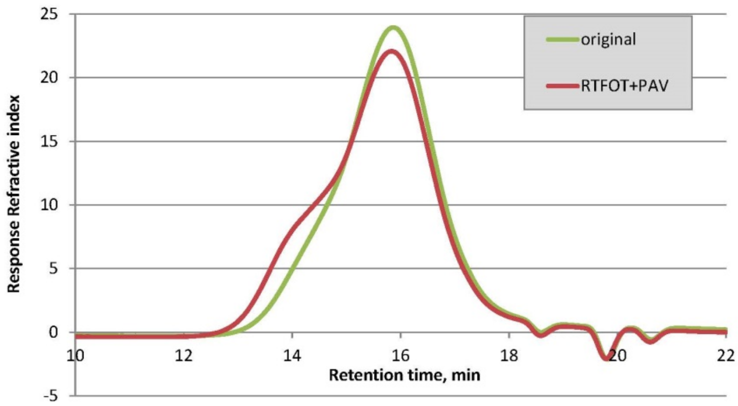
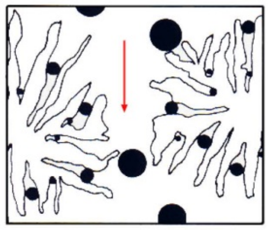
Accelarated aging

5. Chemical changes, GPC:



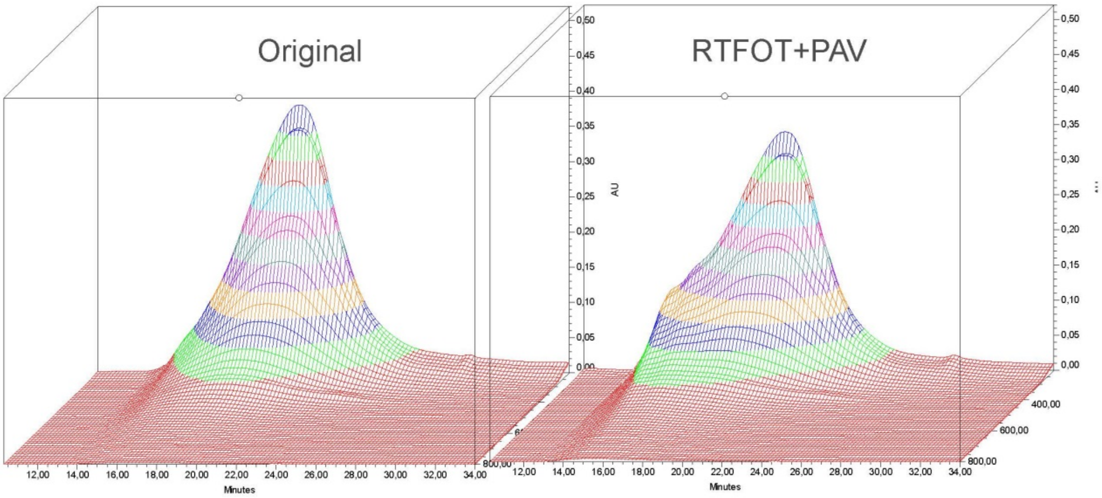


Separation based on molecular size (ideally)

9

Accelarated aging

6. Chemical changes, GPC: uv-vis absorptions



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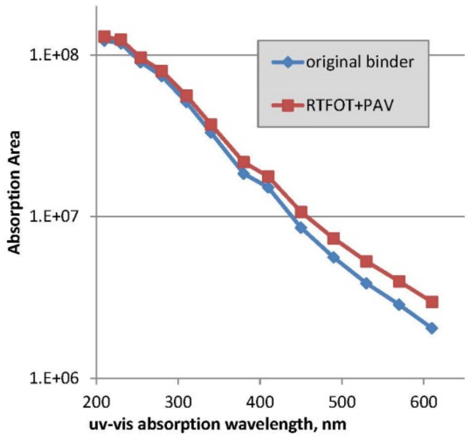
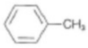
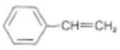
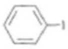
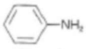
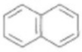
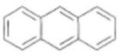
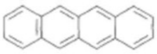
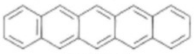
Accelarated aging

6. Chemical changes; uv-vis absorptions



Effects of Structure on Electronic Absorption Corresponding to the Benzenoid Band

Compound	λ_{max}, nm[a]	ϵ_{max}
	255	230
	261	300
	282	450
	256	800
	280	1,430
	314	316
	380	7,900
 (naphthacene)	480	11,000
 (pentacene)	580	12,600

[a]Mostly in ethanol solution

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Accelarated aging

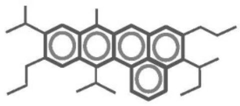
Conclusions accelarated aging (RTFOT+PAV):

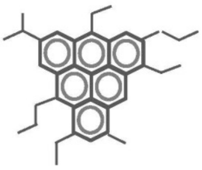
Mechanical:

-decreased temperature sensitivity, more structured black curve
-decreased LVE region at the same stiffness level
-changes in fatigue behavior

Chemical:

-more C=O, more C=C, more S=O, some hydrogen bonding
-increase in (apparent) molecular weight
-increase in larger conjugated aromats
-higher total acid number (TAN)





Ongoing activities:

Difference between RTFOT and PAV, aging temperature
Low temperature fracture properties
Aging index – how to quantify

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Aging temperature

Qualitative measurements mainly using FT-IR:

1. Straigth disstilled binder v/s an oxidized binder (obtained in a refinery process, temp. is 240°C)
2. An original binder aged during PAV 60°C - 10 days
3. An original binder that is dark aged at room temperature (20°C) (2 years)

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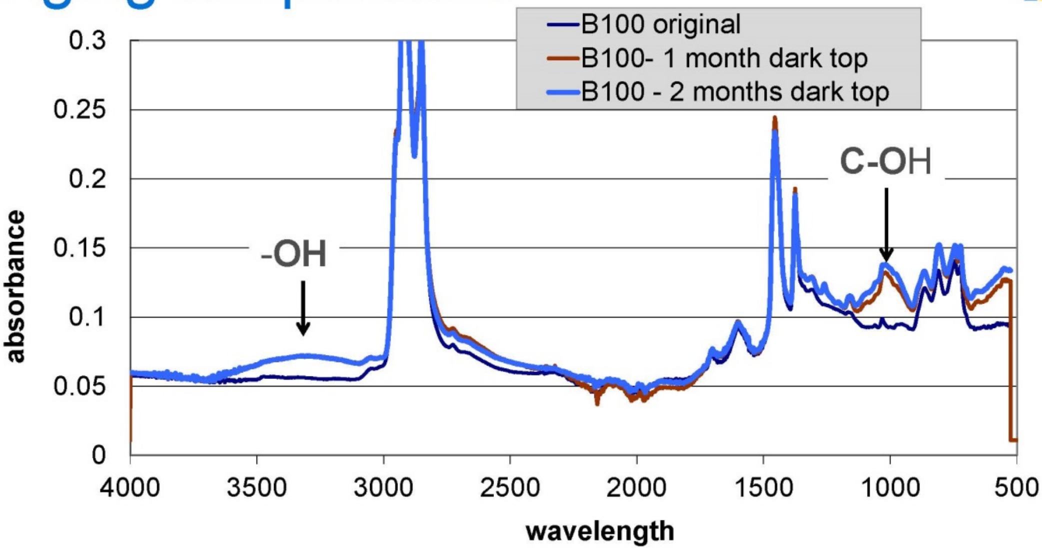
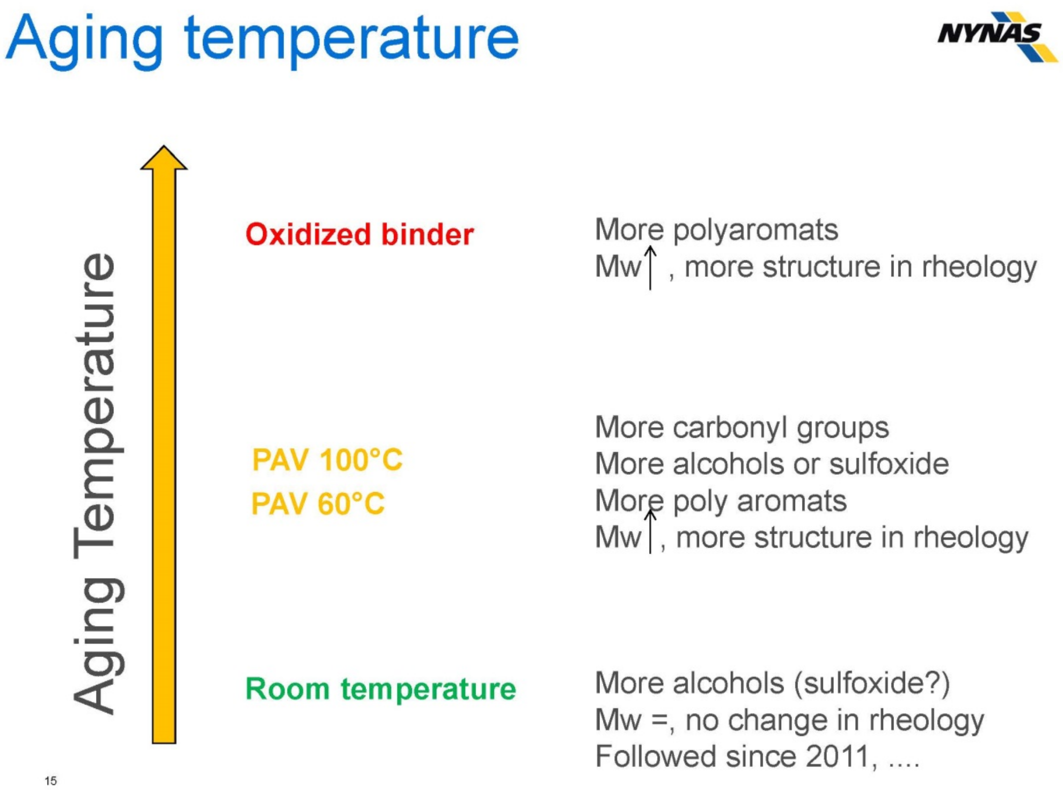
Aging temperature



Dark aging - room temperature:

no formation of carbonyl groups, no increase in aromaticity; increased hydrogen bonding and an increased signal at 1000 cm^{-1}

14


Aging temperature
NYNAS
Aging Temperature
Oxidized binder
More polyaromats
Mw↑ , more structure in rheology
PAV 100°C
PAV 60°C
More carbonyl groups
More alcohols or sulfoxide
More poly aromats
Mw↑, more structure in rheology
Room temperature
More alcohols (sulfoxide?)
Mw =, no change in rheology
Followed since 2011, ...
15

NYNAS

PART II: Field aging & recovered binders:

- **Long Lasting Asphalt Pavements and Bitumen Ageing** *Xiaohu Lu , Per Redelius , Hilde Soenen , Mikael Thau,* E&E conference 2012

- **Durability of Polymer Modified Binders in Asphalt Pavements**, *Xiaohu Lu, Hilde Soenen, Serge Heyrman, Per Redelius,* ISAP conference 2014

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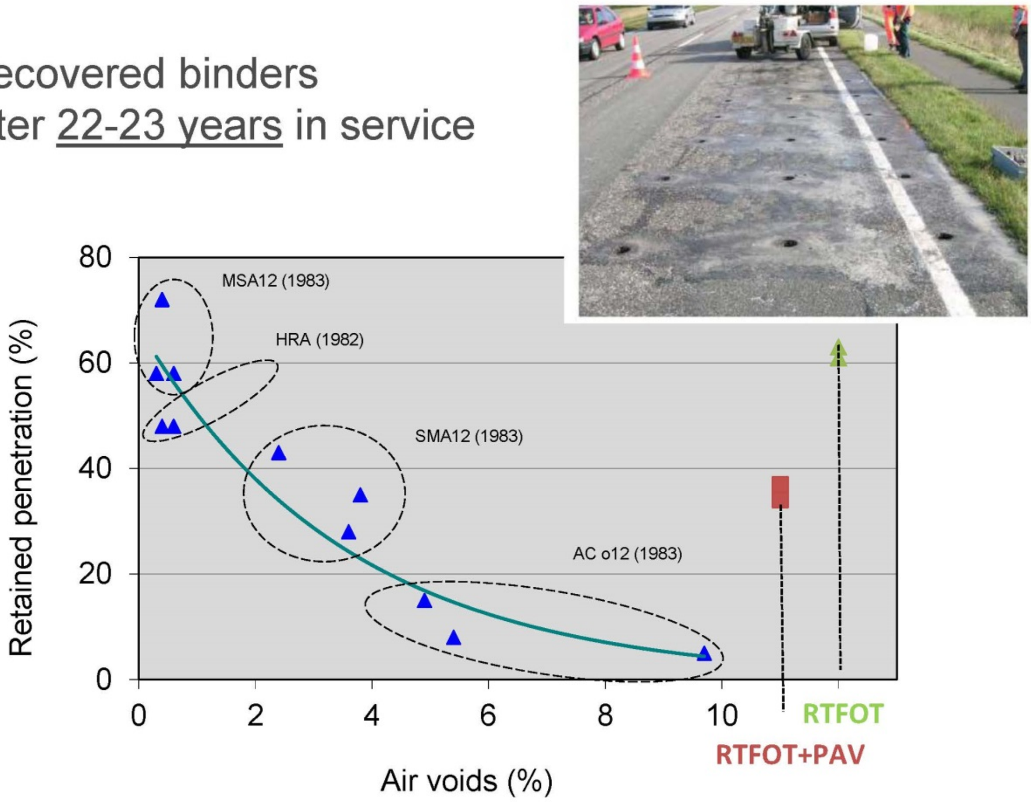
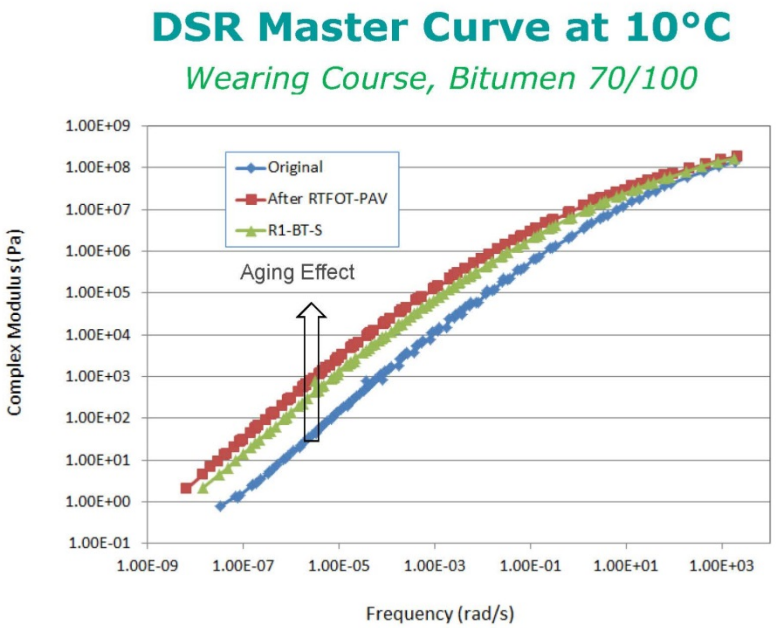
Recovered binders after 22-23 years in service



Recovered binders – 6 years in the field (air voids ~ 1%)



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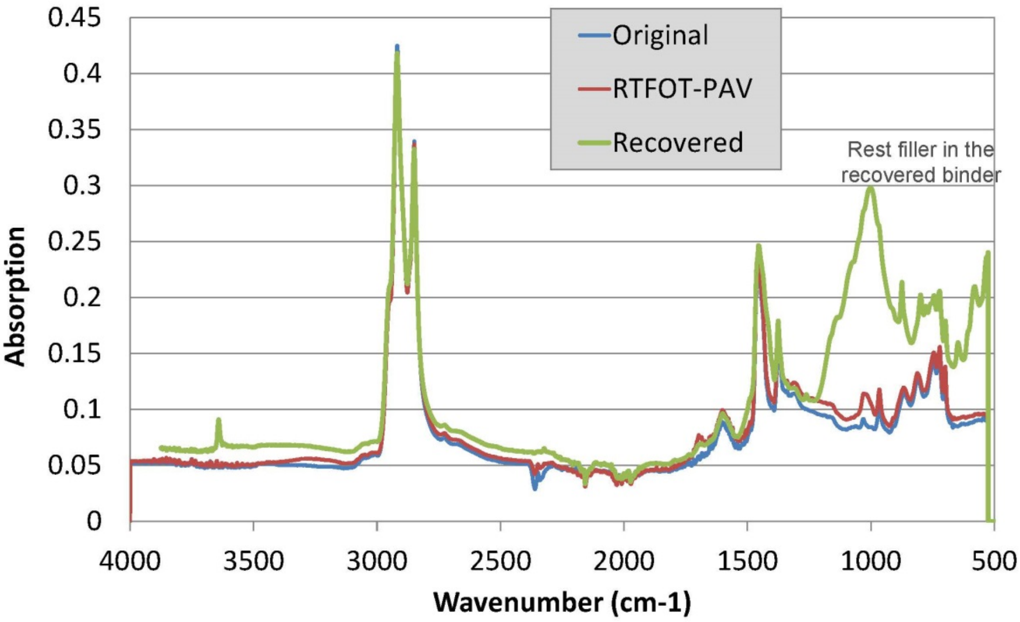
Further analysis of recovered binders:



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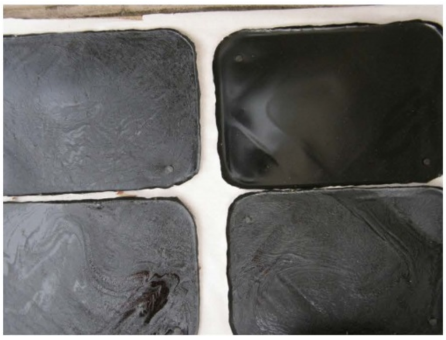
PART III: Bitumen films left outside:

Two sets of bitumen samples were placed outside for 1 year:

- One set got as much sun as possible
- Another set without direct sun light

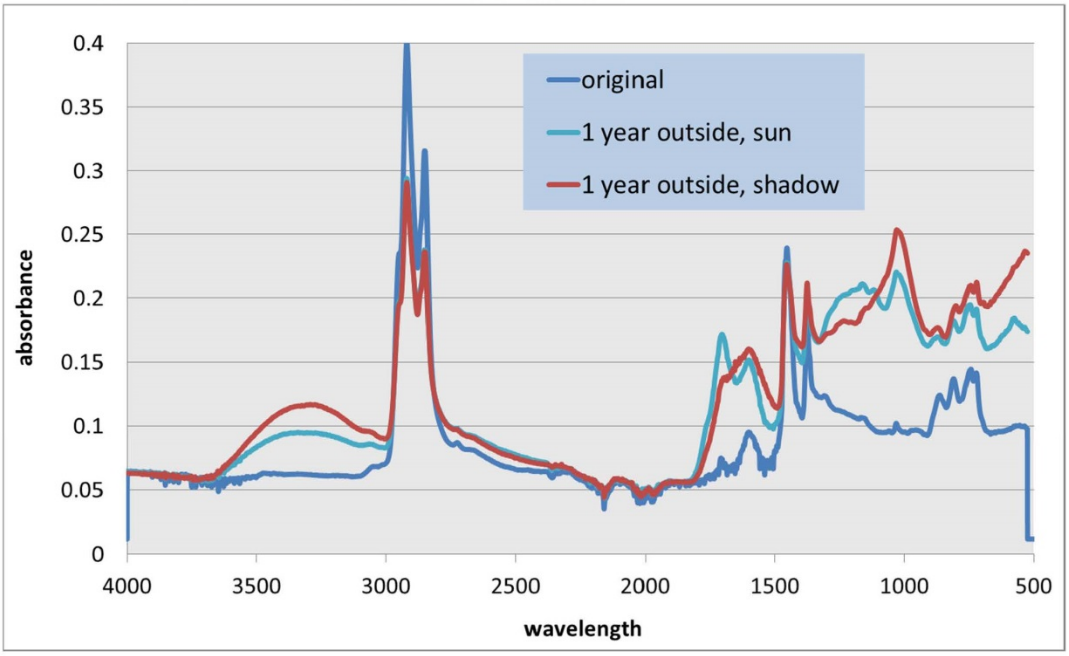
After 1 week:



After 1 year:

20

Bitumen films left outside :



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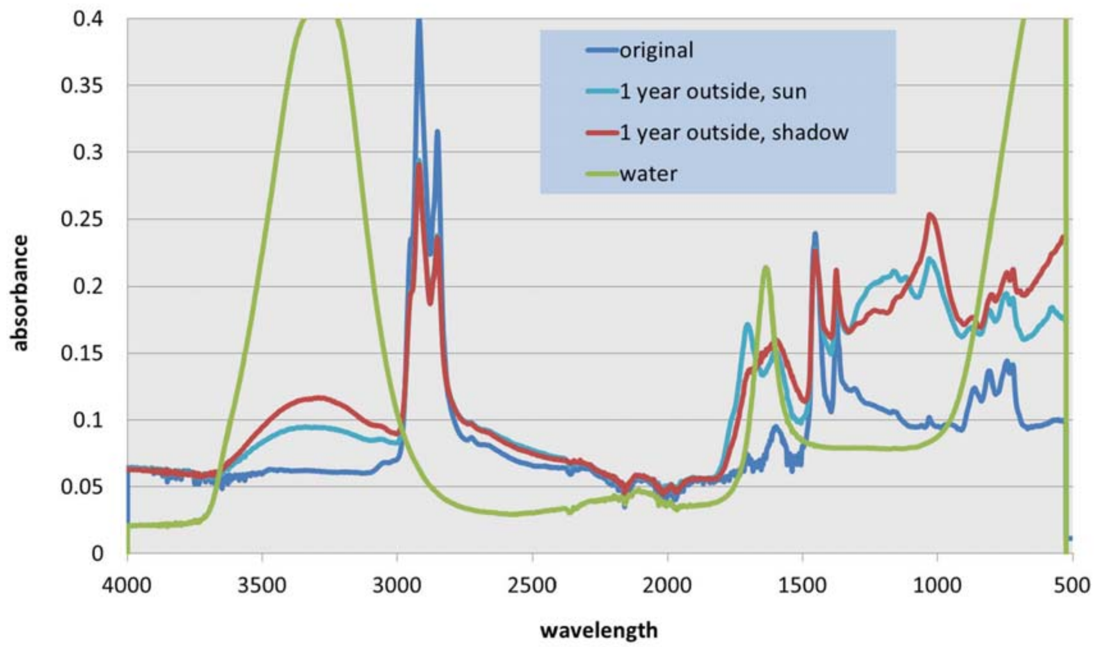
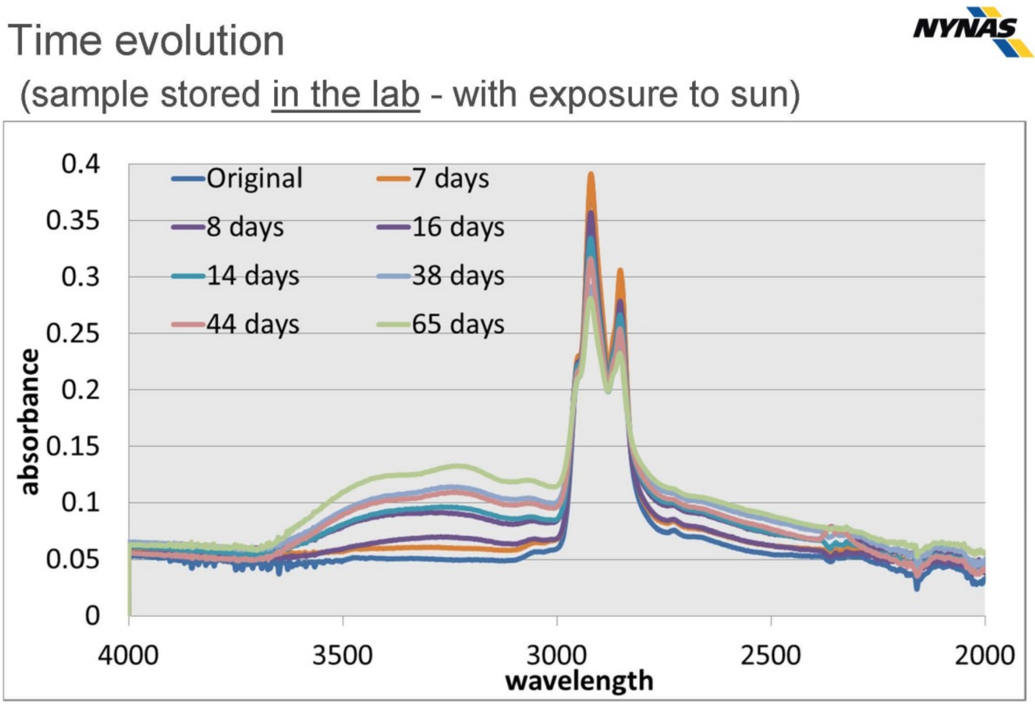
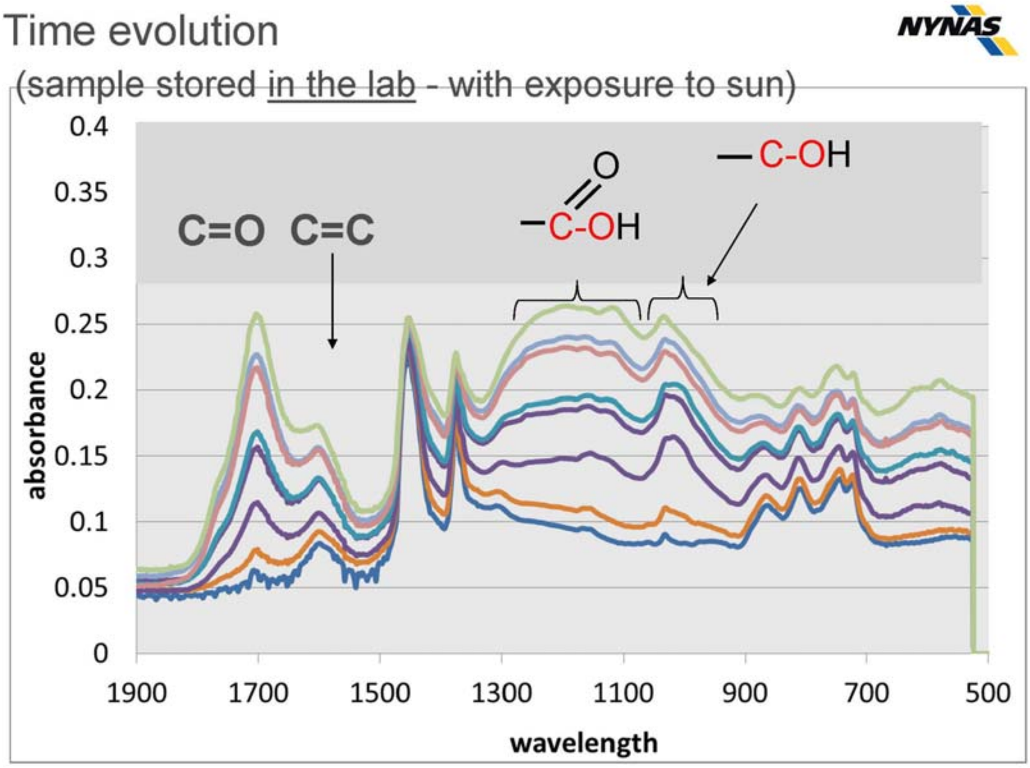
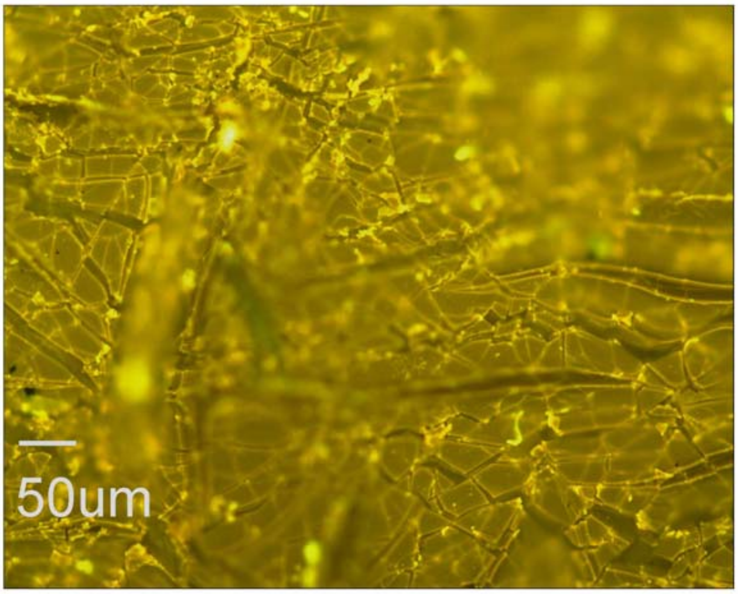
Water?




Time evolution
(sample stored in the lab - with exposure to sun)
NYNAS
Original
7 days
8 days
16 days
14 days
38 days
44 days
65 days
absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
4000
3500
3000
2500
2000
wavelength


Time evolution
(sample stored in the lab - with exposure to sun)
C=O C=C
O
—C-OH
—C-OH
absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1900
1700
1500
1300
1100
900
700
500
wavelength

Microscopy, lab aged after 8 months
200x magnification



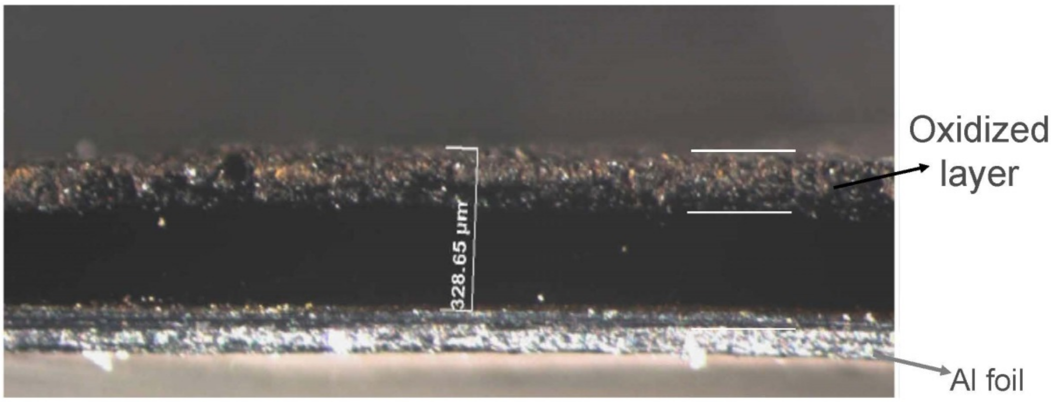
-No loading
-No temp. fluctuations

NYNAS

Macrotome & microscopy measurements:

Made at Ansers, Louvain La Neuve, Belgium

Visual observations: Color change after oxidation,
Thickness indication of aged layer is ≥ 120 um. (1 year outside)



Conclusions:

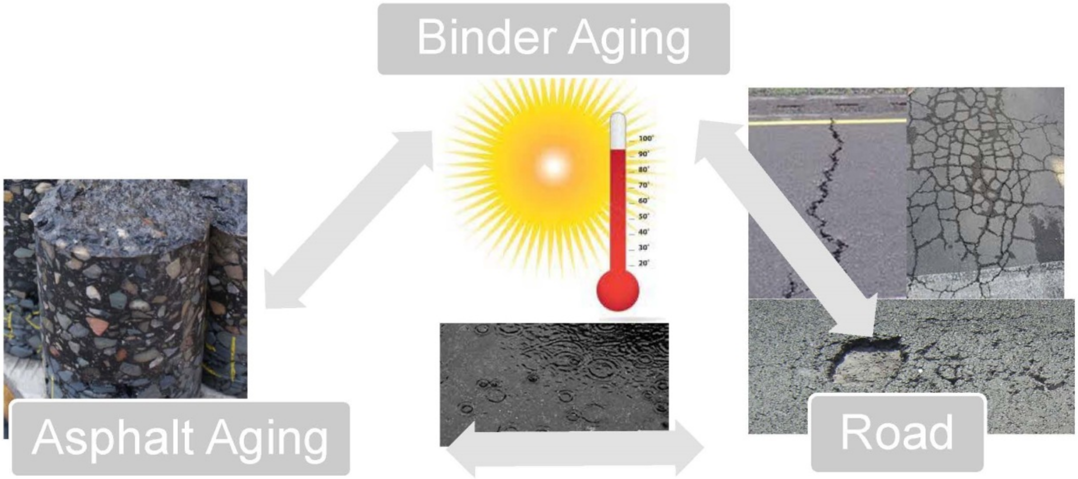
RTFOT + PAV: Similar changes in rheolgical properties
Chemical reactions seem similar as in field aging
Can predict aging for low airvoids (2-4%) pavements

PAV: Open pavements need longer PAV tests
Aging index – what parameter?
Influence of UV light? (raveling, crack initiation top down?)
Influence of aging on adhesion stone-bitumen and water sensitivity?

27

Aging :

Which asphalt property deteriorates (first) due to binder aging:
Low temperature cracking? Raveling? Fatigue cracking?
Perform asphalt tests, on aged asphalt specimen (aged in compacted form).



28

8.4 Ronald Blab, University of Vienna, How to understand field aging of bitumen - recent experimental and modeling efforts

TECHNISCHE UNIVERSITÄT WIEN
Vienna University of Technology

HOW TO UNDERSTAND FIELD AGEING OF BITUMEN - RECENT EXPERIMENTAL AND MODELING EFFORTS

Ronald Blab, Bernhard Hofko, Lukas Eberhardsteiner,
Josef Füssl, Daniel Steiner,
Florian Handle, Markus Hospodka, Hinrich Grothe

Workshop on Bitumen Ageing,
TU Delft, September 2014

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Outline

- **Bitumen Microstructure & Field Ageing Mechanism**
- Micromechanical Modeling of Binder (Ageing)
- Comparison of Field and Lab Ageing

 ISBN 978-94-6186-524-3

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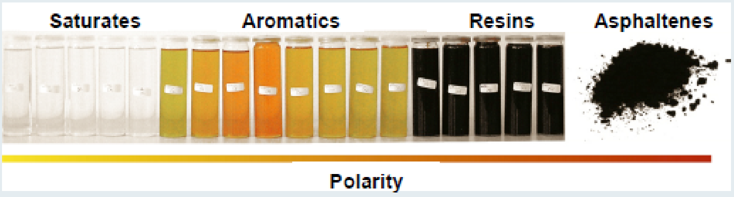
Bitumen Composition - SARA



- Most common concept to identify constituents of bitumen = **SARA**
- **Asphaltenes** → n-heptane non soluble
- **Maltenes** → n-heptane soluble
- Further separation of Maltenes by chromatographic separation → Saturates, Aromatics, Resins

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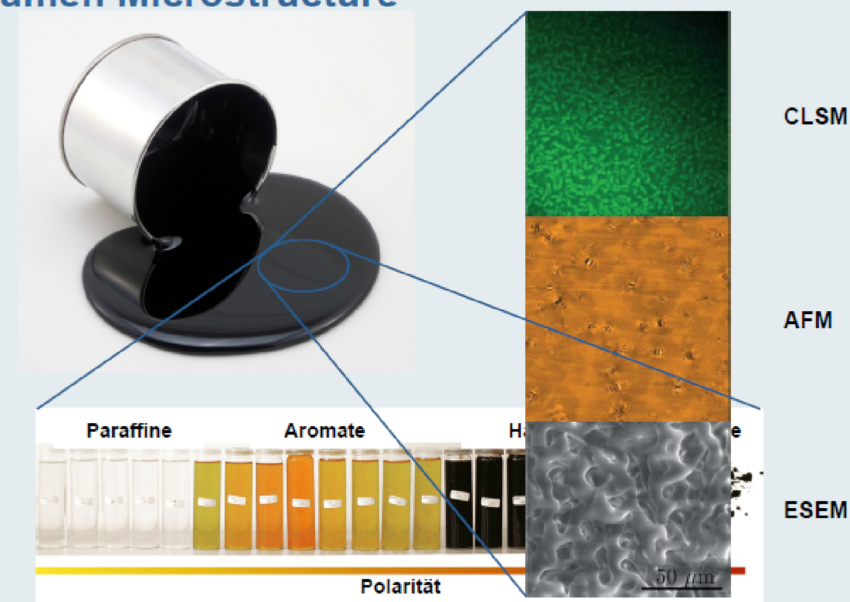
Bitumen Microstructure



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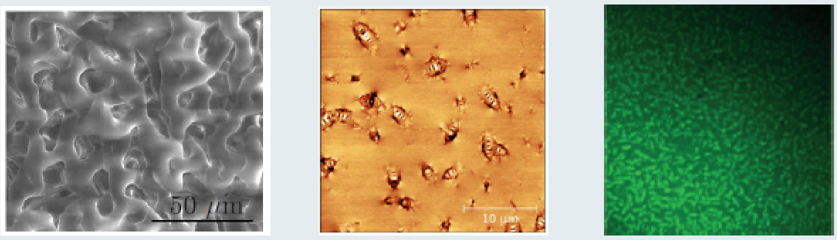
Bitumen Microstructure



Source: Sayeda Nahar, TU Delft

- Imageing methods to detect microstructure
  - Environmental Scanning Electron Microscopy (ESEM)
  - Atomic Force Microscopy (AFM)
  - Confocal Laser Scanning Microscopy (CLSM)
  - …
- **Micelle structures embedded within a matrix** – different thesis

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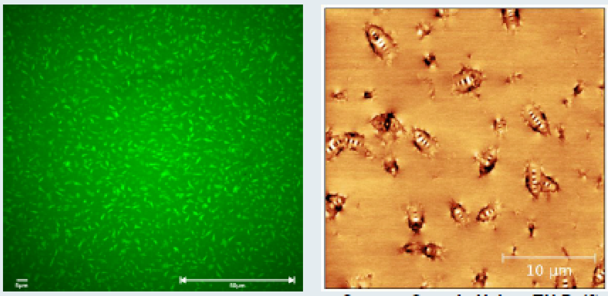
Bitumen Microstructure



Source: Sayeda Nahar, TU Delft

Micro Phase: **2 respective 3 phases distinguishable**
Catana Phase (bees)
Mantle Phase
Matrix

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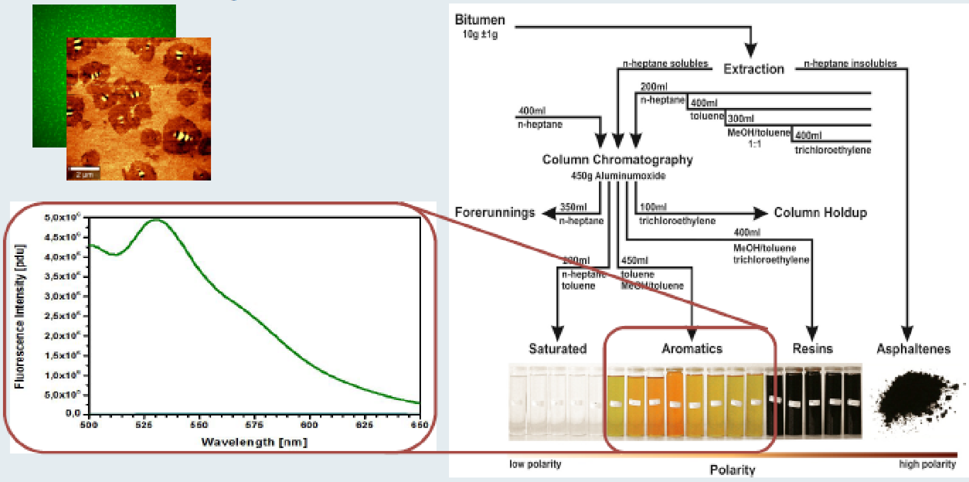
Bitumen Microstructure

Identification of phases



spectroscopy & chromatography
fluorescence comes from „Aromatics“

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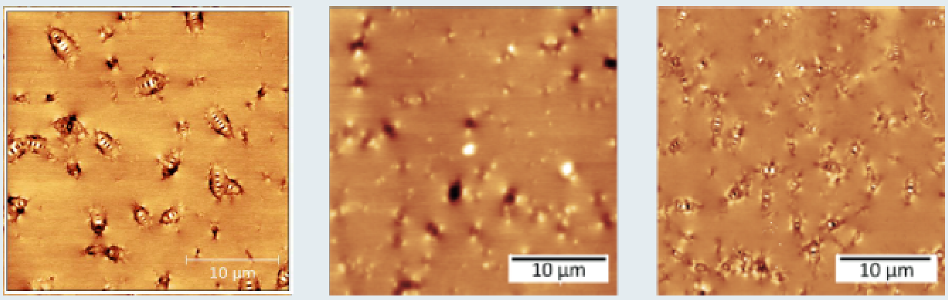
Bitumen Microstructure

Identification of phases

- chromatographic separation of distillation bitumen 70/100 by **n-Heptan-precipitation**
- seperation of asphaltens (non soluble) and maltens (soluble)
- AFM analysis of origin and artificial bitumen with different asphalten content



origin bitumen 10,2% asphaltens | **malten phase without asphaltens** | **artificial bitumen 10 % asphaltens**

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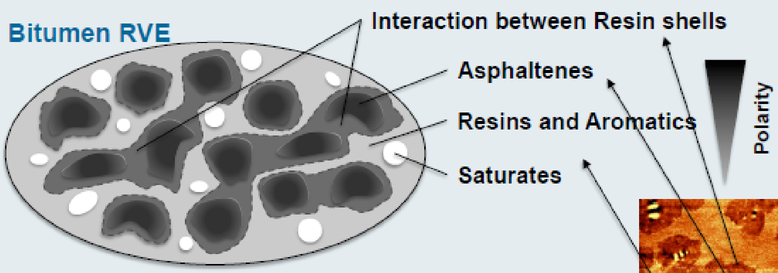
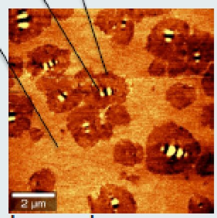
Bitumen Microstructure





- Assumption for present research in Vienna
  - Matrix (Maltenes)
  - Micelles (Asphaltene core + shell of highly polar resins + aromatics)
    - strongly contributing to stiffness
    - shell to balance polarity gap between maltene phase and asphaltenes – homogeneous dispersion

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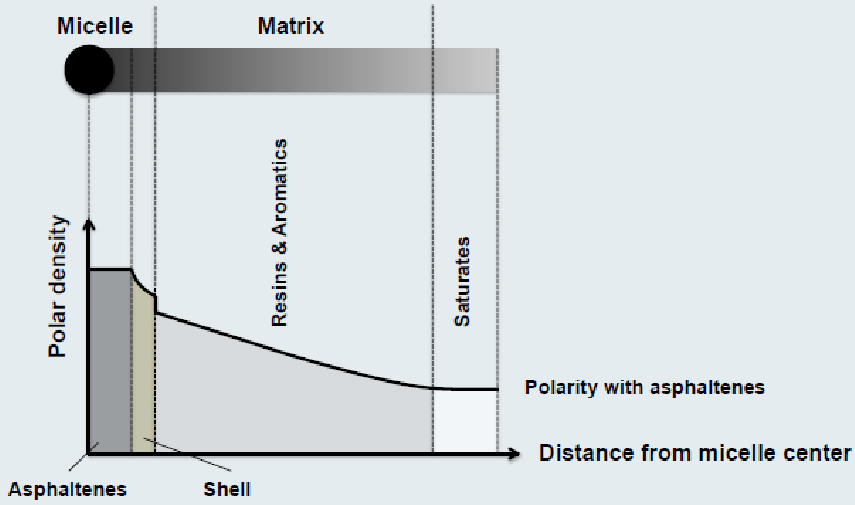
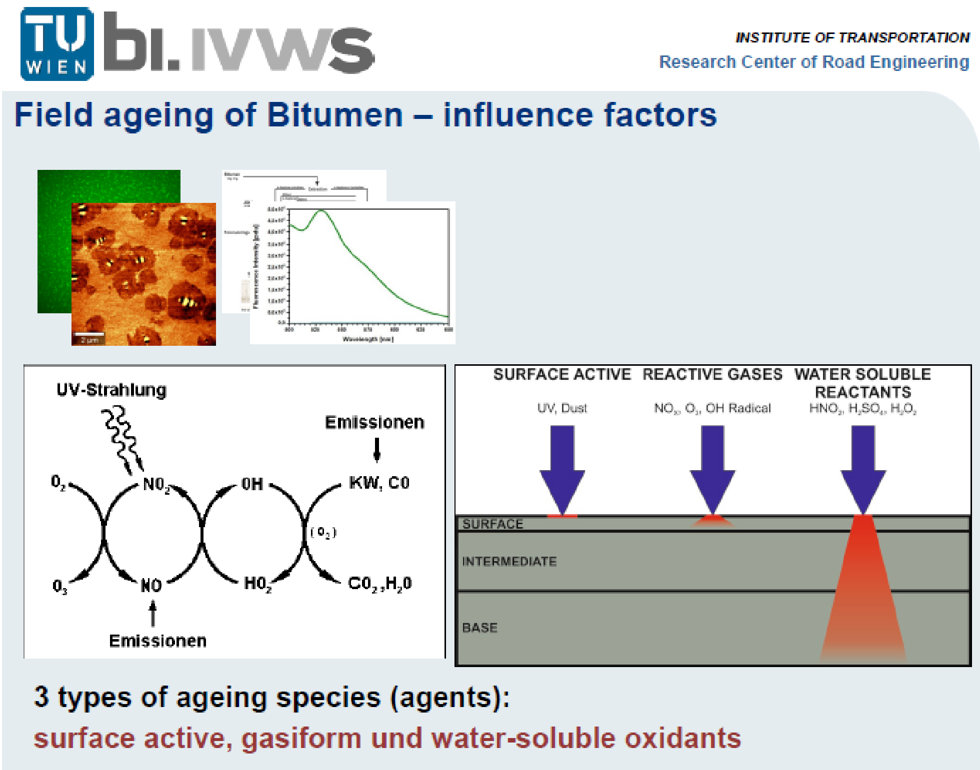
Bitumen Microstructure

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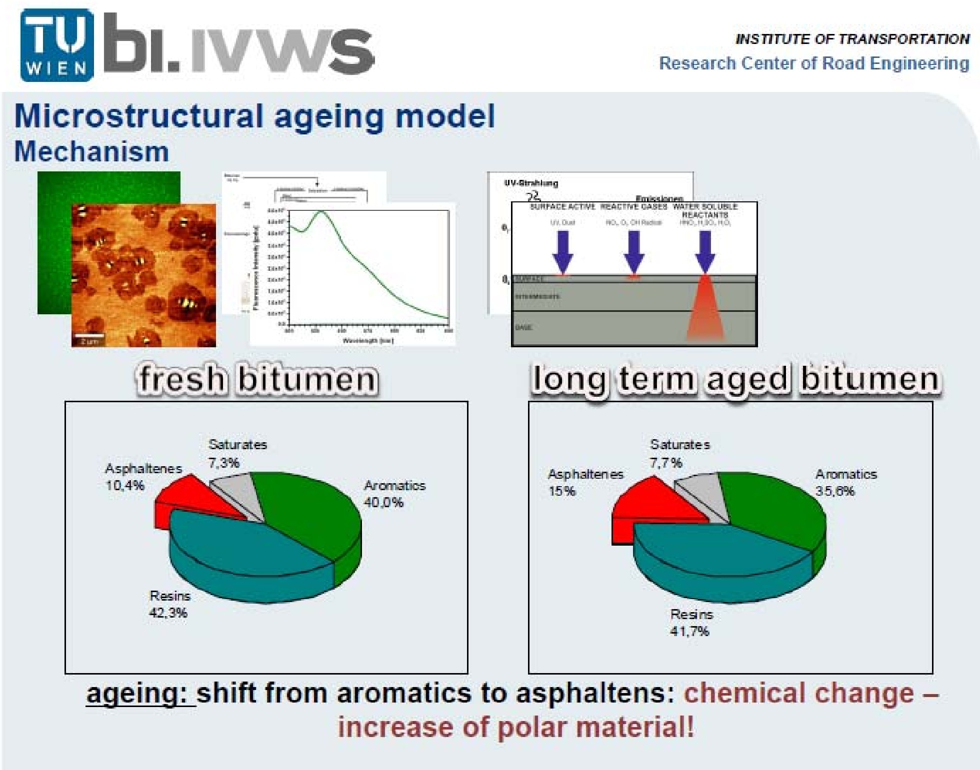
Field ageing of Bitumen – influence factors
UV-Strahlung
Emissionen
O_2 NO_2 OH KW, CO
(O_2)
O_3 NO HO_2 CO_2, H_2O
Emissionen
SURFACE ACTIVE
UV, Dust
REACTIVE GASES
NO_x, O_3, OH Radical
WATER SOLUBLE REACTANTS
HNO_3, H_2SO_4, H_2O_2
SURFACE
INTERMEDIATE
BASE
3 types of ageing species (agents):
surface active, gasiform und water-soluble oxidants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Microstructural ageing model
Mechanism
fresh bitumen
long term aged bitumen
Saturates 7,3%
Asphaltenes 10,4%
Aromatics 40,0%
Resins 42,3%
Saturates 7,7%
Asphaltenes 15%
Aromatics 35,6%
Resins 41,7%
ageing: shift from aromatics to asphaltens: chemical change – increase of polar material!

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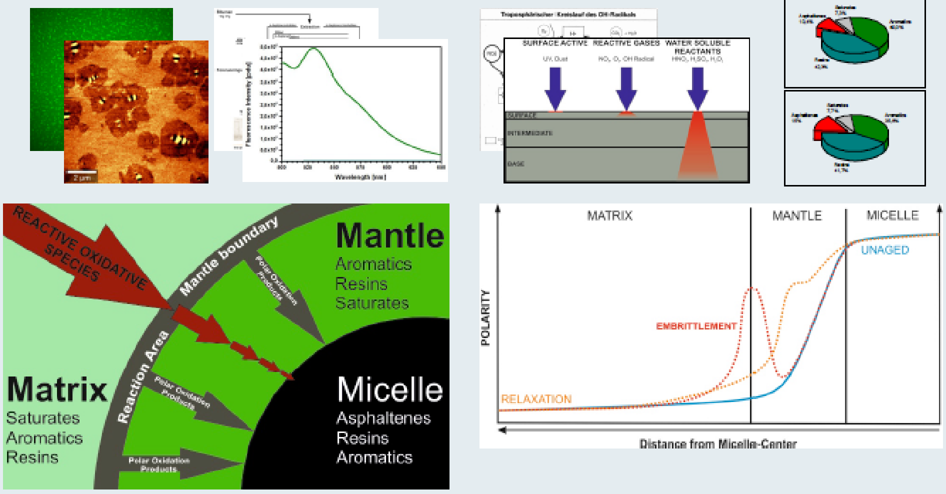
Microstructural ageing model

Mechanism



oxidative species reacts at the mantel boundary and leads to embrittlement (ageing), polar oxitation products can be transported to the micelle in dependence of temperature (healing)

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Conclusion

- Improved **model of the bitumen micro structure** based on combined chemical and modern image analyzing procedures
- Identification of different **field ageing species**
- **Field ageing mechanism**: reactive oxidative species lead to an embrittlement of bitumen due to a shift of the polarity gradient in the mantle boundary between micelle and matrix (shell structure)
- „**Healing"- effects** result from a re-organization of the polar oxidation products from the mantle into the micelle

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Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M., S. Nahar, A. Schmets, A. Scarpas: *Microstructure and Rheology of Bitumen - Friends or Foes?*, Materials and Structures, 2014 (submitted)

Handle F., Eberhardsteiner L., Füssl J., Hofko B., Hospodka M., Blab R., Grothe H.: *The Bitumen Microstructure – A Fluorescent Approach, Materials and Structures*, 2014 (submitted)

Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: *Recent Developments in the Field of Ageing of Bitumen and Asphalt Mixes*, Transport Research Record, 2015 (submitted)

Handle F., Eberhardsteiner L., Füssl J., Hofko B., Hospodka M., Blab R., Grothe H.: *Understanding the Microstructure of Bitumen: a CLSM and Fluorescence Approach to Model Bitumen Ageing Behavior*, 12th ISAP International Conference on Asphalt Pavements, Raleigh, 2014

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Outline

- ❑ Bitumen Microstructure & Field Ageing Mechanism
- ❑ **Micromechanical Modeling of Binder (Ageing)**
- ❑ Comparison of Field and Lab Ageing

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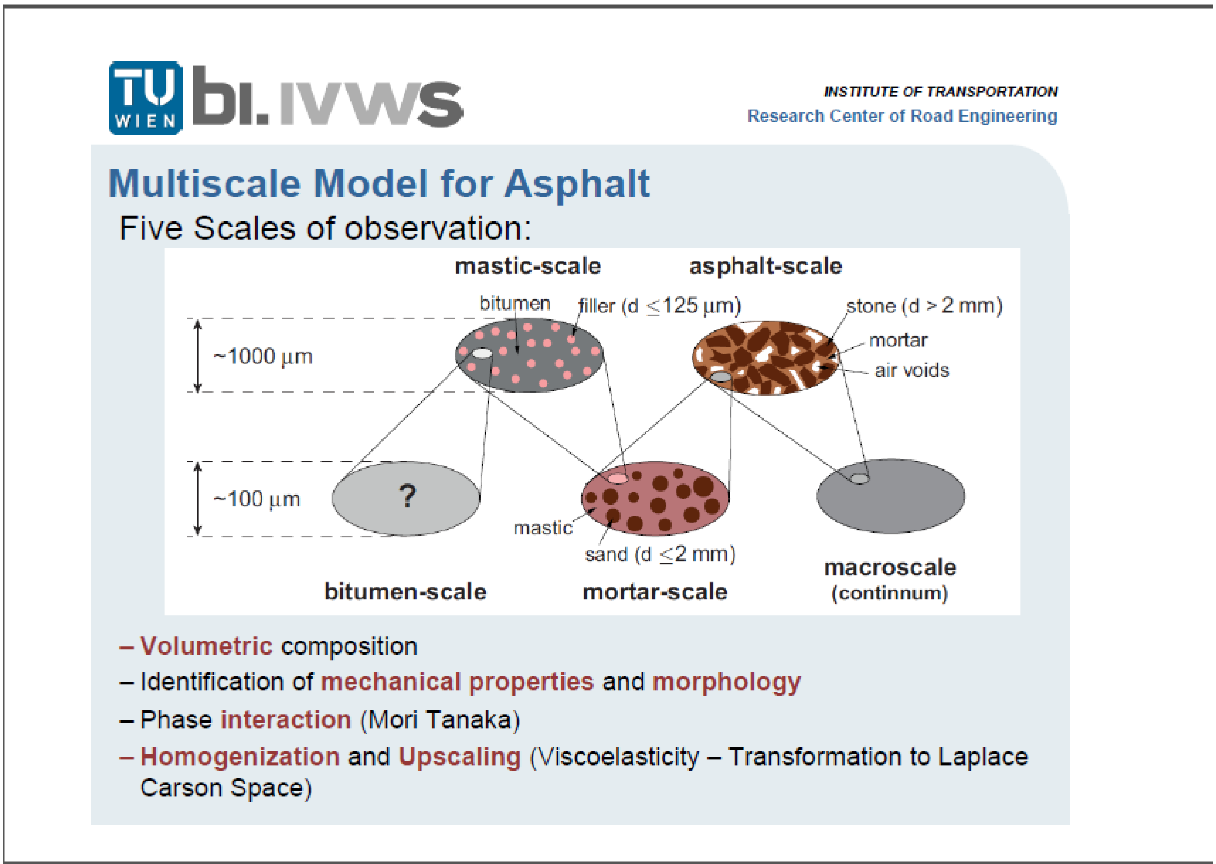
Motivation for Multiscale Modeling

- macroscopic material models
  identified material parameters applicable to *one* specific mixture consisting of *one* specific bitumen (e.g., B70/100), *one* specific filler (e.g. limestone dust) and *one* specific aggregate
- (bottom-up) multiscale models
  material parameters as functions of composition (mix design), morphology, and the properties of the material phases (e.g., bitumen, filler, ...)

⇨ applicable to several asphalt mixes
⇨ consideration of changes in material behavior at respective scale of observation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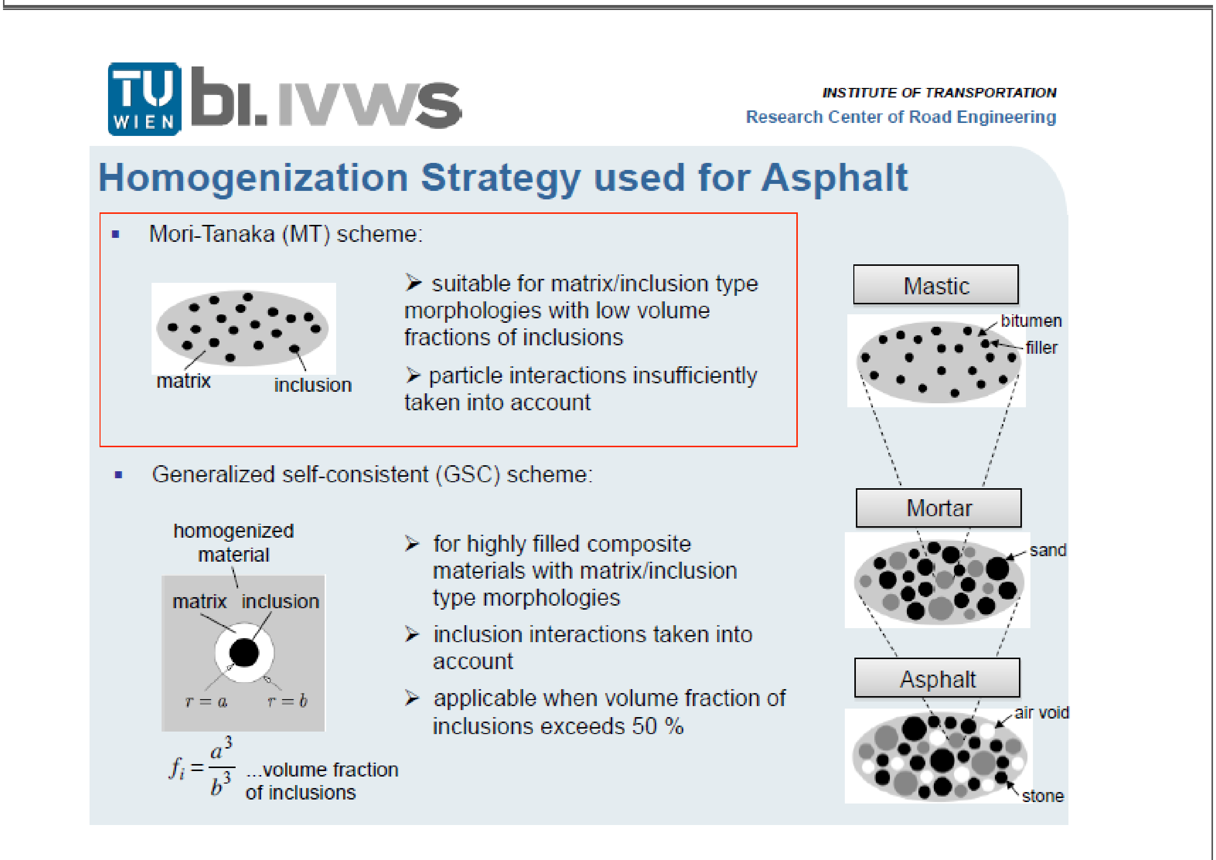
Multiscale Model for Asphalt
Five Scales of observation:
mastic-scale
asphalt-scale
bitumen
filler (d ≤125 µm)
stone (d > 2 mm)
mortar
air voids
~1000 µm
~100 µm
?
mastic
sand (d ≤2 mm)
bitumen-scale
mortar-scale
macroscale (continnum)
– Volumetric composition
– Identification of mechanical properties and morphology
– Phase interaction (Mori Tanaka)
– Homogenization and Upscaling (Viscoelasticity – Transformation to Laplace Carson Space)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Homogenization Strategy used for Asphalt
Mori-Tanaka (MT) scheme:
matrix
inclusion
suitable for matrix/inclusion type morphologies with low volume fractions of inclusions
particle interactions insufficiently taken into account
Generalized self-consistent (GSC) scheme:
homogenized material
matrix
inclusion
r = a
r = b
$f_i = \frac{a^3}{b^3}$ ...volume fraction of inclusions
for highly filled composite materials with matrix/inclusion type morphologies
inclusion interactions taken into account
applicable when volume fraction of inclusions exceeds 50 %
Mastic
bitumen
filler
Mortar
sand
Asphalt
air void
stone

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Micromechanical Modelling of Binder Ageing

- **Set-up** of micromechanical model
- **Identification** of mechanical behavior of material phases
  - Maltenes
  - Asphaltenes + Shell
- **Validation** of model for un-aged binder

- Mechanical behavior of **lab-aged binder** (RTFOT+PAV)
- **Validation** of model for lab-aged binders

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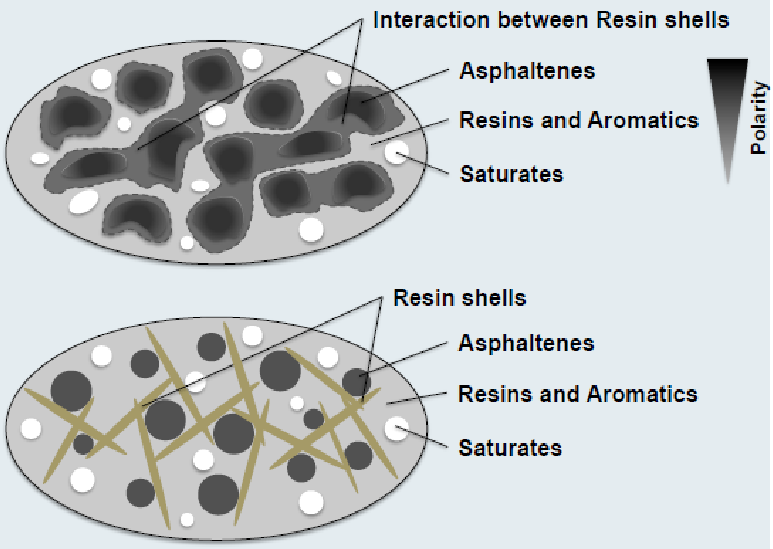
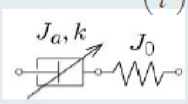
Micromechanical Model



Micro-mechanical Model

$$J(t) = J_0 + J_a\left(\frac{t}{\tau}\right)^k$$



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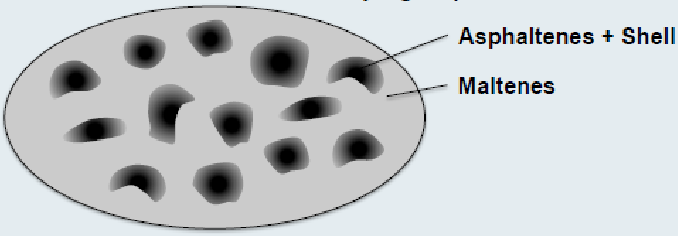
Identification experiments

- Binder: 70/100 pen

Parameter	70/100 pen
Penetration [1/10 mm]	90.9
Softening Point Ring & Ball [°C]	46.7
SHRP PG [°C]	58-22

- Artificial bitumens with varying asphaltene contents



- Creep-Recovery tests at different temperatures

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Experimental Layout

Identification Maltenes
+ Effect of Temperature (Arrhenius)

Asphaltene content		Test temperature -5 °C	+5 °C	+15 °C
0 wt. %	0 vol-%	•	•	•
5 wt. %	4.18 vol-%	•	•	•
10 wt. %	7.77 vol-%		•	
15 wt. %	12.32 vol-%		•	•
20 wt. %	17.36 vol-%		•	
30 wt. %	26.71 vol-%		•	

Validation

Identification Asphaltenes

Identification Interaction Shell

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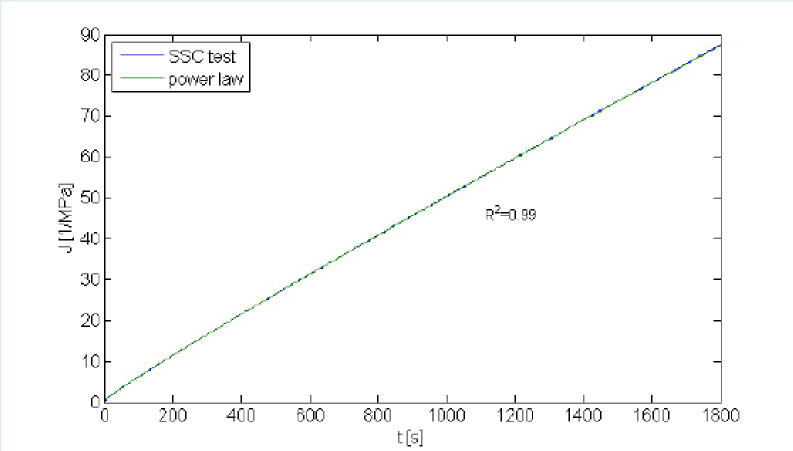
Identification Maltenes



	-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

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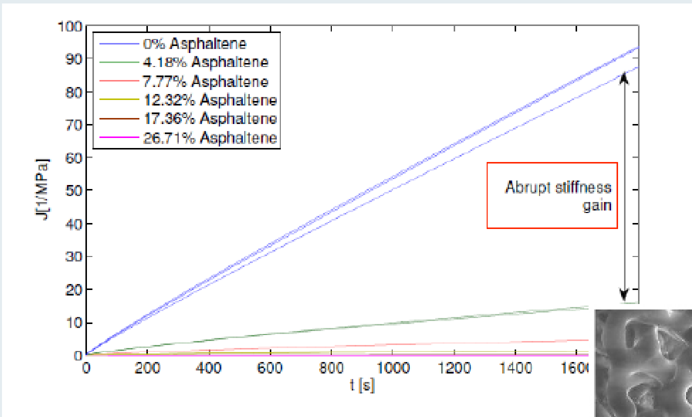
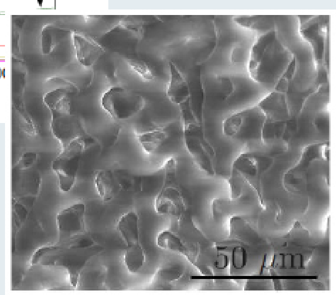
Identification Asphaltenes + Shell





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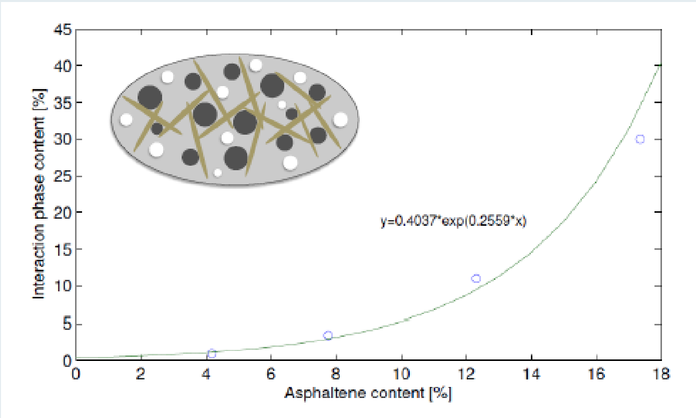
Identification Asphaltenes + Shell



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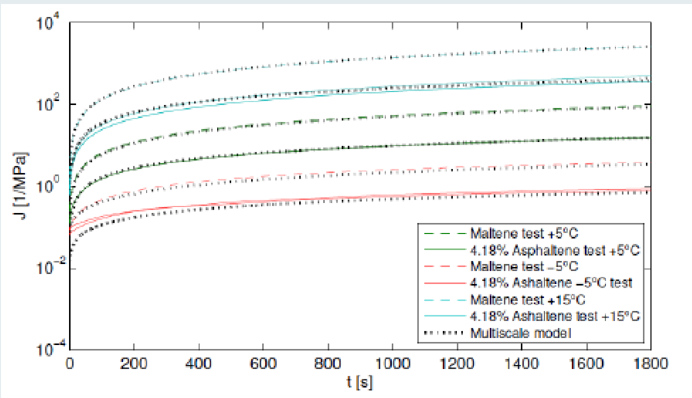
Model Validation



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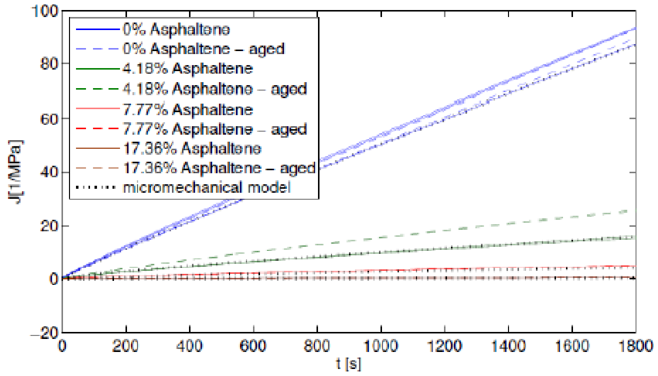
Mechanical Behavior of Lab-aged Binders

Asphaltene content	Test temperature		
	-5 °C	+5 °C	+15 °C
0 %	•/○	•/○	•/○
4.18 %	•/○	•/○	•/○
7.77 %	○	•/○	○
12.32 %		•	•
17.36 %	○	•/○	○
26.71 %		•	

tumen, ○ . . . tests on aged bitumen



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Conclusion

- **Power-law model** describes viscoelastic behavior of bitumen constituents well
- **Identification** of mechanical behavior of maltenes, asphaltenes and interaction of micelle shells **successfully**
- Abrupt gain in stiffness with addition of asphaltenes to maltene phase → **Micelle-Matrix Model including interacting shells**
- **Correlation** between interaction of micelle **shells** (needles) and **asphaltene** content
- No difference between un-aged and lab-aged binder
  - in maltene/asphaltene behavior
  - in interaction of micelle shells
- **Change in asphaltene content sufficient** to explain change in mechanical behavior due to **ageing**

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Eberhardsteiner L., Füssl J., Hofko B., Handle F., Hospodka M., Blab R., Grothe H.: *Influence of asphaltene content on mechanical bitumen behavior – Experimental investigation and micromechanical modeling.* Materials and Structures, 2014, DOI: 10.1617/s11527-014-0383-7

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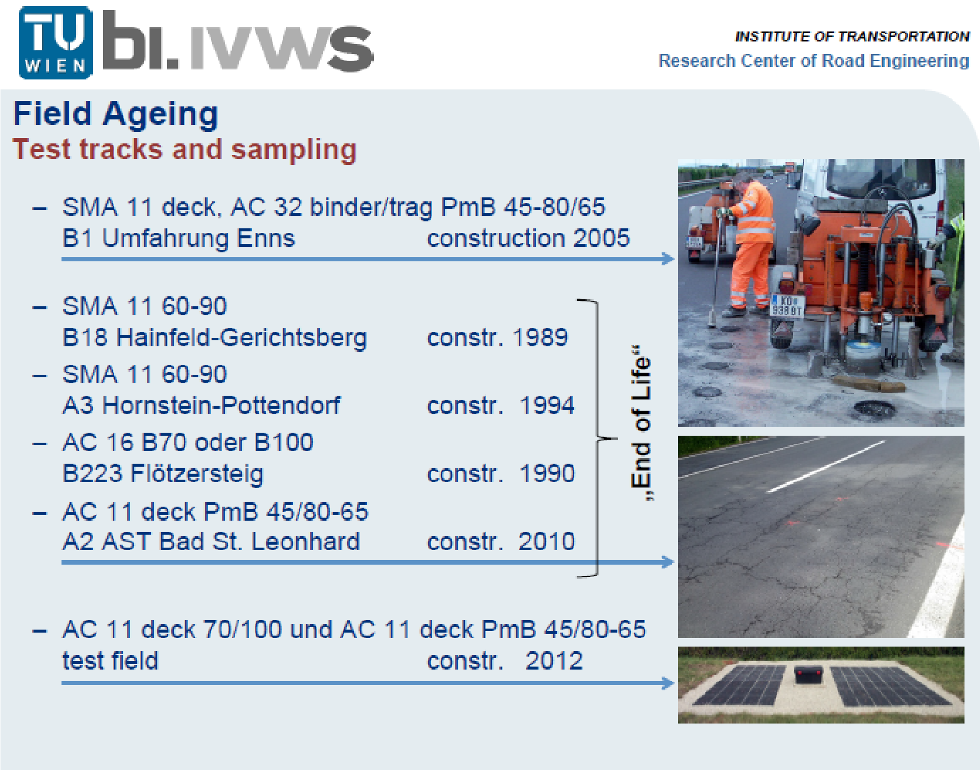
Outline

- Bitumen Microstructure & Field Ageing Mechanism
- Micromechanical Modeling of Binder (Ageing)
- **Field and Lab Ageing**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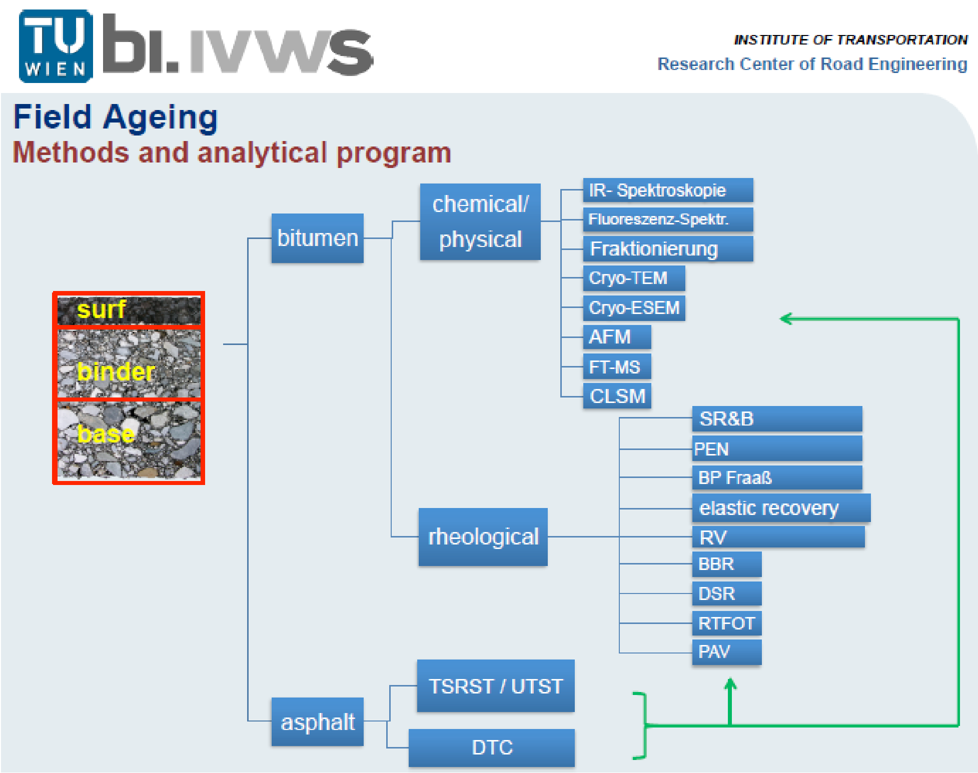
Field Ageing
Test tracks and sampling
– SMA 11 deck, AC 32 binder/trag PmB 45-80/65
B1 Umfahrung Enns construction 2005
– SMA 11 60-90
B18 Hainfeld-Gerichtsberg constr. 1989
– SMA 11 60-90
A3 Hornstein-Pottendorf constr. 1994
– AC 16 B70 oder B100
B223 Flötzersteig constr. 1990
– AC 11 deck PmB 45/80-65
A2 AST Bad St. Leonhard constr. 2010
„End of Life“
– AC 11 deck 70/100 und AC 11 deck PmB 45/80-65
test field constr. 2012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Field Ageing
Methods and analytical program
surf
binder
base
bitumen
chemical/ physical
IR- Spektroskopie
Fluoreszenz-Spektr.
Fraktionierung
Cryo-TEM
Cryo-ESEM
AFM
FT-MS
CLSM
rheological
SR&B
PEN
BP Fraaß
elastic recovery
RV
BBR
DSR
RTFOT
PAV
asphalt
TSRST / UTST
DTC

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Field ageing
Results bitumen

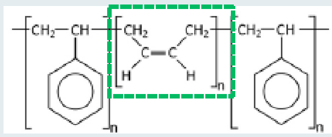
– Bitumen recoverd from base and binder course show almost identical rheological parameter after 10 years → recycling!

– Long term ageing of bitumen is very much restricted to **surface course**

– **Comparison of field and lab ageing indicates**

• RTFOT	rheological	☑
	chemical	☑
• RTFOT+PAV	rheological	☑
	chemical	☒
	SBS-degeneration	☒

• Butadien binding is sensitive to UV-radiation



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Field Ageing
Bitumen - alternative Lab Test for long term ageing

PAV: high pressure (21 bar) and temperatures (100°C) do not simulate field ageing mechanism

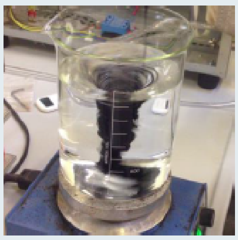
Liquid phase ageing

high concentration of OH radicals

(3-6 vol.%- H_2O_2 solution)

• **treatment of R&B specimens**
→ uneven bitumen surface

• **dropping and steering of hot bitumen in H_2O_2 solution**
→ clumping of bitumen sample



under construction

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Field ageing
HMA - Alternative Lab Test for long term ageing

Existing lab-ageing procedures

handicaps

- Loose HMA
- High pressure
- High temperature

objective:

- compacted HMA specimen
- field surface temperature and pressure
- high concentrations of highly reactant gaseous agents

Alterungsmethode	Temp. [°C]	Dauer [h]	Probeart	DIN EN	Veröffentlichung	Jahr	Alterung durch
Short-Term Oven Ageing (STOA)	135	8-36	loses Material	-	NCHRP	1988	-
Long-Term Oven Ageing (LTOA)	85	120	verdichtete PK	-	NCHRP	1988	-
Low-Pressure Oxidation (LPA)	60, 85	120	verdichtete PK	-	SHRP	1989	Sauerstoff (1,9 l/min)
Rotating Cylinder Aging Test (RCAT)	70 - 100	144	Asphaltmastix	15323	Verhasselt & Choquet	1991	Sauerstoff (4,5 l/h)
Long-Term Ageing	60	48	verdichtete PK	-	NCHRP	1988	
	60	120 - 240	verdichtete PK	-	NCHRP	1988	Druck (0,7 MPa) Luft
	107	72	verdichtete PK	-	NCHRP	1988	
Bitutest-Protocol	135	2	loses Material	-	Scholz (PhD-Thesis) Nottingham	1995	-
	85	120	verdichtete PK	-	Scholz (PhD-Thesis) Nottingham	1995	-
Ottawa Sand Mixtures	163	variiert	verdichtete PK	-	AAPT	1952	-
	60	1200	verdichtete PK	-	AAPT	1952	-
Plancher et al.	150	5	verdichtete PK	-	AAPT	1976	-
Hugo & Kennedy	100	96, 168	-	-	AAPT	1985	80 % relative Luftfeuchtigkeit
Khalid & Walsh	60	bis 600	verdichtete PK	-	EE Congr.	2000	Luft (3 l/min)
Kumar & Goetz	60	24-240	verdichtete PK	-	AAPT	1977	Luft Wasser
Kim et al.	60	24-120	verdichtete PK	-	Oregon	1988	Druck (0,7 Mpa) Luft
Pressure Ageing Vessel	100	72	verdichtete PK	14769	EE Congr.	1996	Druck (2,07 Mpa) Luft
Saturation Ageing tensile stiffness conditioning Test (SATS)	85	65	verdichtete PK	12697-45	Transport 157	2004	Wasser Druck
Modelltopf nach Potschka	140	1	loses Material	-	FA 07.121 G95 E		Luft 20%Sauerstoff 80%Stickstoff
Braunschweiger Alterung (BSA)	80	96	loses Material	-	FE 07.208/2004/BGB 2007	2007	Luft
Wamboldscher Alterungstisch	40	720 - 1440	verdichtete PK	-	Diss. Wambold	1996	Luft UV Licht
Alterung im Wärmeschrank	135-175	4-24	loses Material	-	Bitumen 2/1999	1999	Luft Stickstoff
Bochumer Alterungsverfahren BAV	100	72	verdichtete PK	-	Cetinkaya (Diss.) Bochum	2011	Erwärmte Druckluft
Wheatherometer Delft	-20 - +60	1,2,3,4, 6,8,10,12	verdichtete PK	-	Hagos (PhD-Thesis) Delft	2008 2011	Weather-Ometer UV Licht Luftfeuchtigkeit NaCl
BRRC long term Re road	60	24, 72, 216, 336	loses Material	-	journal of wuhan university	2010	Sauerstoff (15ml/min)
UV (LCPC) long term	60	336	loses Material	-	journal of wuhan university	2010	UV Licht
Rilem (ISBS - Braunschweig)	85	24, 72, 144, 216	loses Material	-	journal of wuhan university	2010	-
Pr.1-van de ven - circular Steelplate - STA	165	2	Asphaltmastix	-	van de Ven et al. EE congress	2012	-
Pr.1-van de ven - LTA - PAV	80	168	Asphaltmastix	-	van de Ven et al. EE congress	2012	Druck (21 bar)
Pr.1-van de ven - for removal from plate	150	0,5	Asphaltmastix	-	van de Ven et al. EE congress	2012	-
Pr.2-van de ven - STA - oven	135	4	loses Material	-	van de Ven et al. EE congress	2012	-
Pr.2-van de ven - protocol 2 - heated up and compacted	165		loses Material	-	van de Ven et al. EE congress	2012	mechanische Bel.
Pr.2-van de ven - LTA - PAV	70+80	72+96	verdichtete PK	-	van de Ven et al. EE congress	2012	Druck (21 bar)
AASHTO R302 (nchrp) - STA	135	4	loses Material	-	RILEM Advances in [...]Testing [...]of Bituminous Materials	2013	-
c - long-term aging	85	120	verdichtete PK	-	RILEM Advances in [...]Testing [...]of Bituminous Materials	2013	-
Braunschweiger Alterung (BSA)	80	96	loses Material	-	Büchler et al. EE congress	2008	Luft

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Field ageing
HMA - Alternative Lab Test for long term ageing

Viennese Ageing Procedure VAPro

optimize mix design

- durability
- recyclability

Long term aged pavements are more prone to failure by

- low-temperature cracking
- fatigue cracking

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Ageing Procedure for Hot Mix Asphalt Specimen - SETUP
Viennese Ageing Procedure VAPro

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Field Ageing

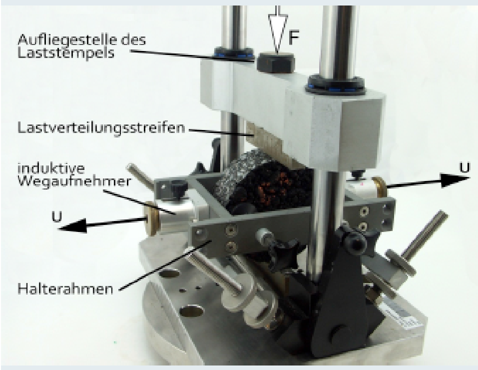
HMA - Alternative Lab Test for long term ageing

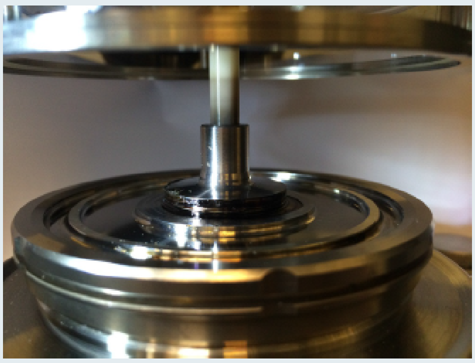
Validation tests - VAPro

Indirect Tensile Test, Cylindrical Sample (IT-CY)

Recovered bitumen DSR

Tests before and after ageing





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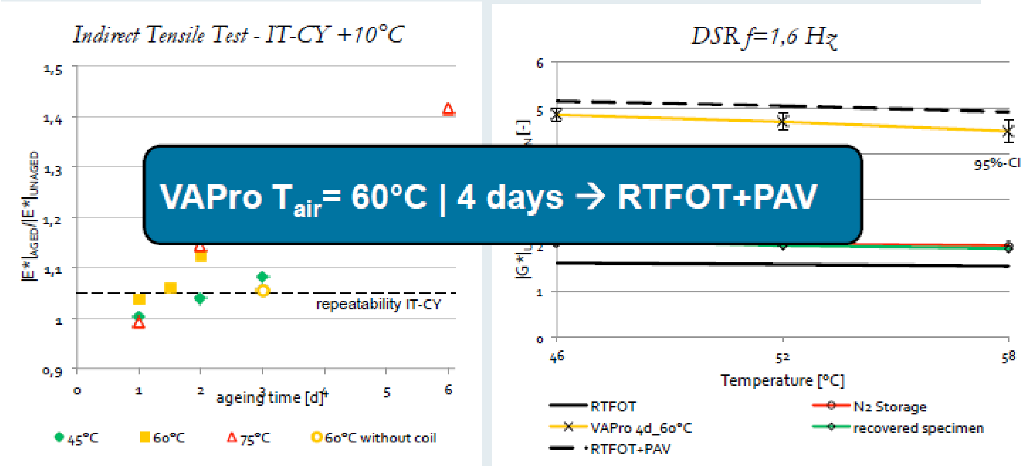
Ageing Procedure for Hot Mix Asphalt Specimen - RESULTS
Viennese Ageing Procedure VAPro

HOT MIX ASPHALT | **BINDER**



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Conclusion

- long term field ageing of bitumen can not be simulated realistically by RTFOT & PAV procedure in the lab
- **Liquid Phase ageing** as alternative bitumen ageing procedure is not practicably yet
- **modified RTFOT** (1-times @ 230°C, 3-times @ 163°C) is recommended instead of RTFOT & PAV procedure to simulate bitumen field ageing
- **Viennese ageing procedure** (VAPro) is appropriate lab method to simulate field ageing of compacted HMA specimens and will be further developed to carry out performance based tests on lab aged HMA specimens

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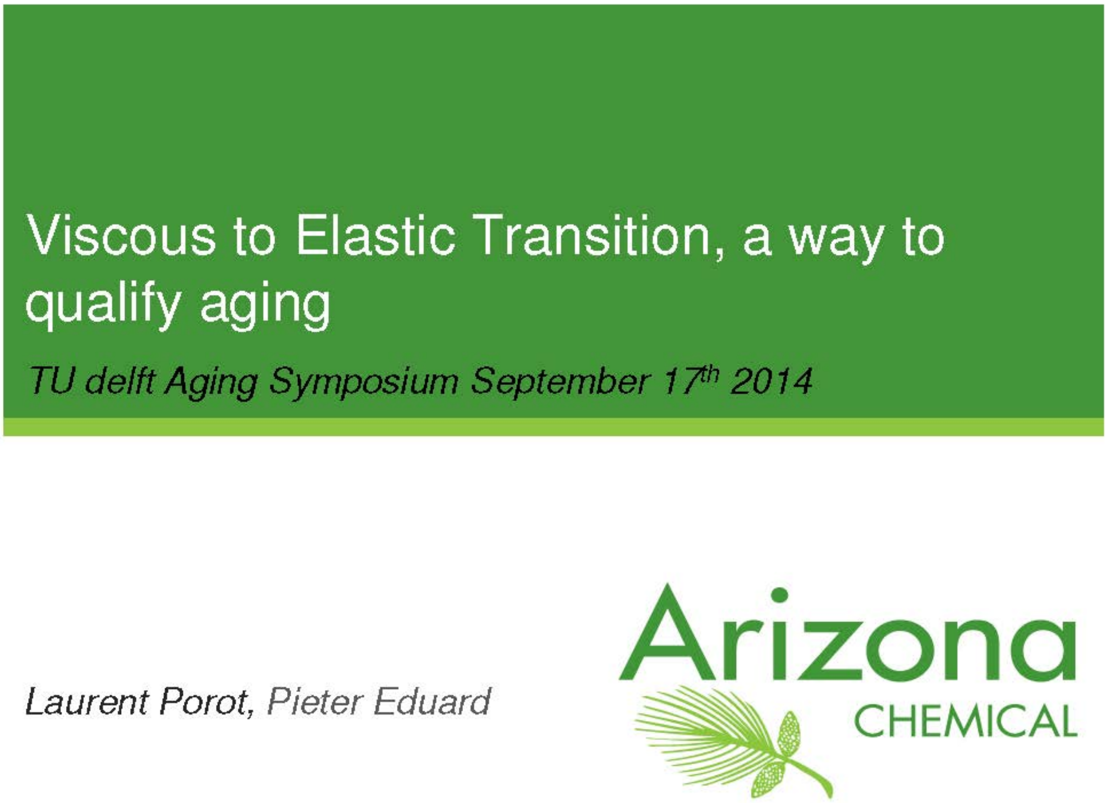
References

Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: *Impact of Field Ageing on Low-Temperature Performance of Binder and Hot Mix Asphalt*, 12th ISAP International Conference on Asphalt Pavements, Raleigh, 2014

Steiner, D., Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: Towards *an efficient laboratory protocol for long-term ageing of compacted asphalt mix specimens*, Transport Research Record, 2015 (submitted)

8.5 Laurent Porot, Arizona Chemical, Viscous to Elastic Transition: a way to qualify aging



Outlines

Arizona CHEMICAL

- Background
- Technical approach
- Status & results
  - Chemical structure FTIR
  - Mechanical properties DSR
- Conclusion

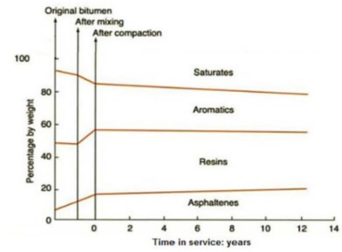
Arizona CHEMICAL

Background

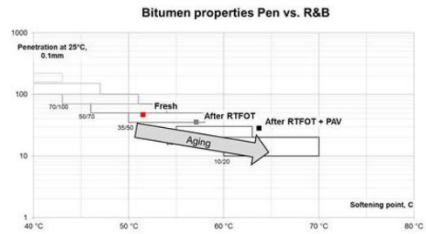
Aging of asphalt binder

Arizona CHEMICAL

- With aging, an asphalt binder changes
  - in microstructure due to oxidation
  - and in properties with hardening



The Shell Bitumen Handbook fifth edition



How to define proper parameters to characterize aging?

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Bitumen aging index

Arizona CHEMICAL

- With aging, hardening can be recorded with
  - Delta softening point, retained penetration
  - Increase of binder modulus*, complex aging coefficient**
  - …

Are these parameters relevant to aging or just hardening?

- FTIR addresses changes in structure
  - Increase of Sulphoxide, Carbonyl ***

How can we better understand the mechanical behavior with an analytical approach?

* ReRoad FP7 project 2012, PARC 2012 Glaser et al **Delaporte et al, Linear viscoelastic properties of bituminous materials, 2007, Journal of the Association of Asphalt Paving Technologists *** Petersen American Chemical Society 1996, TRB Circular E-C140 2009

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Viscous to Elastic Transition

Arizona CHEMICAL

- Rheology can address the viscous elastic behavior of asphalt with
  - Complex Modulus → stiffness
  - Phase angle → visco-elastic behavior
- The Viscous to Elastic Transition* concept
  - When the phase angle equal to 45° ($\tan\delta=1$)
  - Modulus /temperature at VET, "*useful tool to demonstrate the changes in the properties of bituminous materials*"

*Viscous to Elastic Transition temperature of bitumen and the in-situ performance of asphalts, I. Widyatmoko Asphalt 2005
Mapping crack susceptibility of bituminous materials with binder durability, I. Widyatmoko, Rilem 2004

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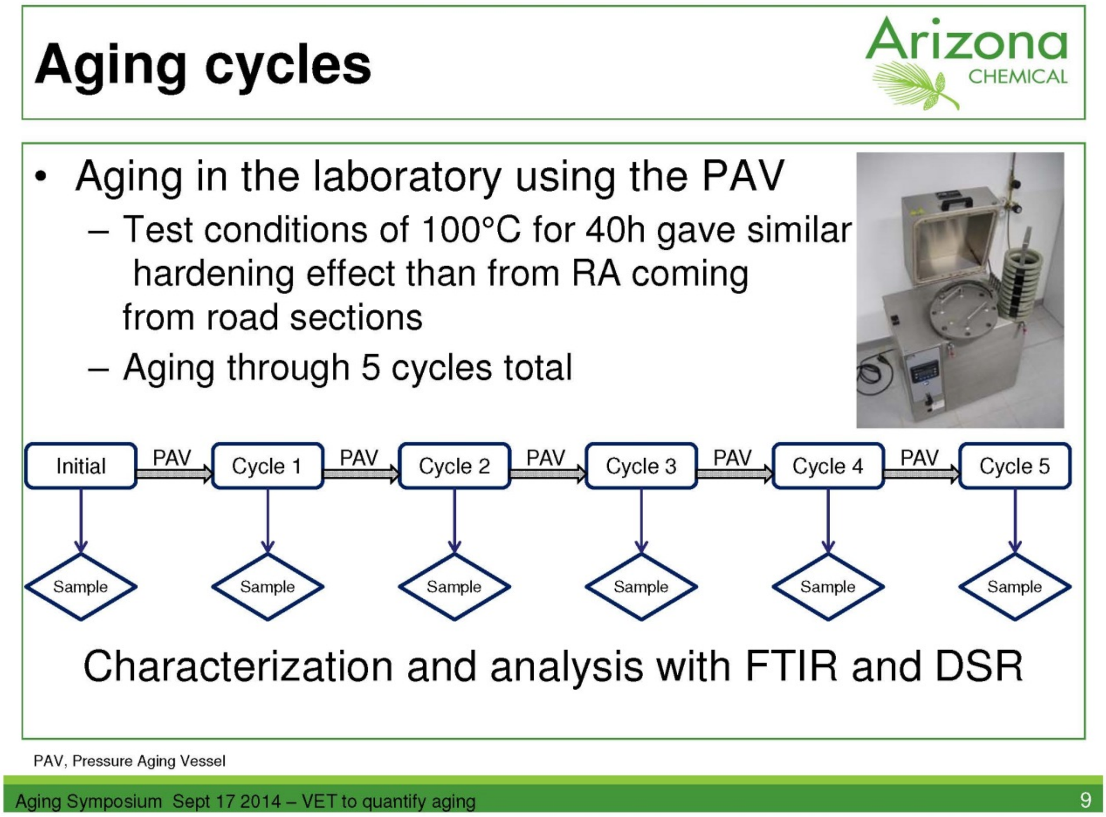
Experimental plan

Technical approach

Arizona CHEMICAL

- Comparing asphalt binders
  - Different binder grades
  - Different binder sources
  - Different binder aging levels through tailored aging cycles
  - Different RA binders recovered from the road
- Looking at the test results from a different angle
  - Basic properties with penetration value and softening point
  - Analytical approach with FTIR
  - Mechanical behavior with DSR


Aging cycles
Arizona CHEMICAL
• Aging in the laboratory using the PAV
– Test conditions of 100°C for 40h gave similar hardening effect than from RA coming from road sections
– Aging through 5 cycles total
Initial
PAV
Cycle 1
PAV
Cycle 2
PAV
Cycle 3
PAV
Cycle 4
PAV
Cycle 5
Sample
Sample
Sample
Sample
Sample
Sample
Characterization and analysis with FTIR and DSR
PAV, Pressure Aging Vessel
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Quantitative FTIR analysis

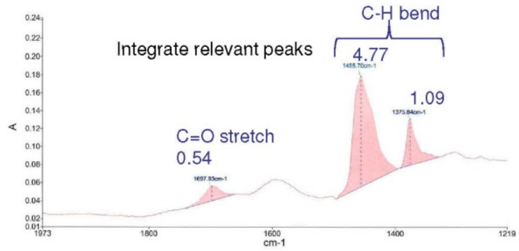
Arizona CHEMICAL

- Quantitative analysis of asphalt binders*
  - Amount of aliphatics → **Unrelated to ageing** 1460 and 1376 cm^{-1}
  - Level of oxidation → **Related to ageing** 1700 and 1030 cm^{-1}

- Calculated ratio
  - Integrated relevant peaks

$ISO = A_{S=O} / A_{C\text{-}H\ bend}$

$ICO = A_{C=O} / A_{C\text{-}H\ bend}$



* W. van den Bergh, *The Effect of Ageing on the Fatigue and Healing Properties of Bitumen*, 2011, Petersen American Chemical Society 1996, TRB Circular E-C140 2009

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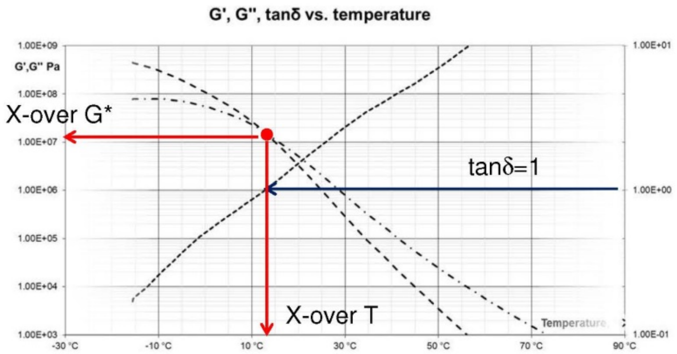
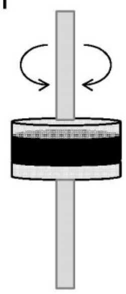
ISBN 978-94-6186-524-3

Viscous to Elastic Transition

Arizona CHEMICAL

- Rheological properties characterized via DSR
  - In Temperature sweep at 1 fixed frequency (10rad/s)
  - Analysis in the range of 10^3 to 10^9 Pa
  - Consider the cross-over properties, G* and T





Results

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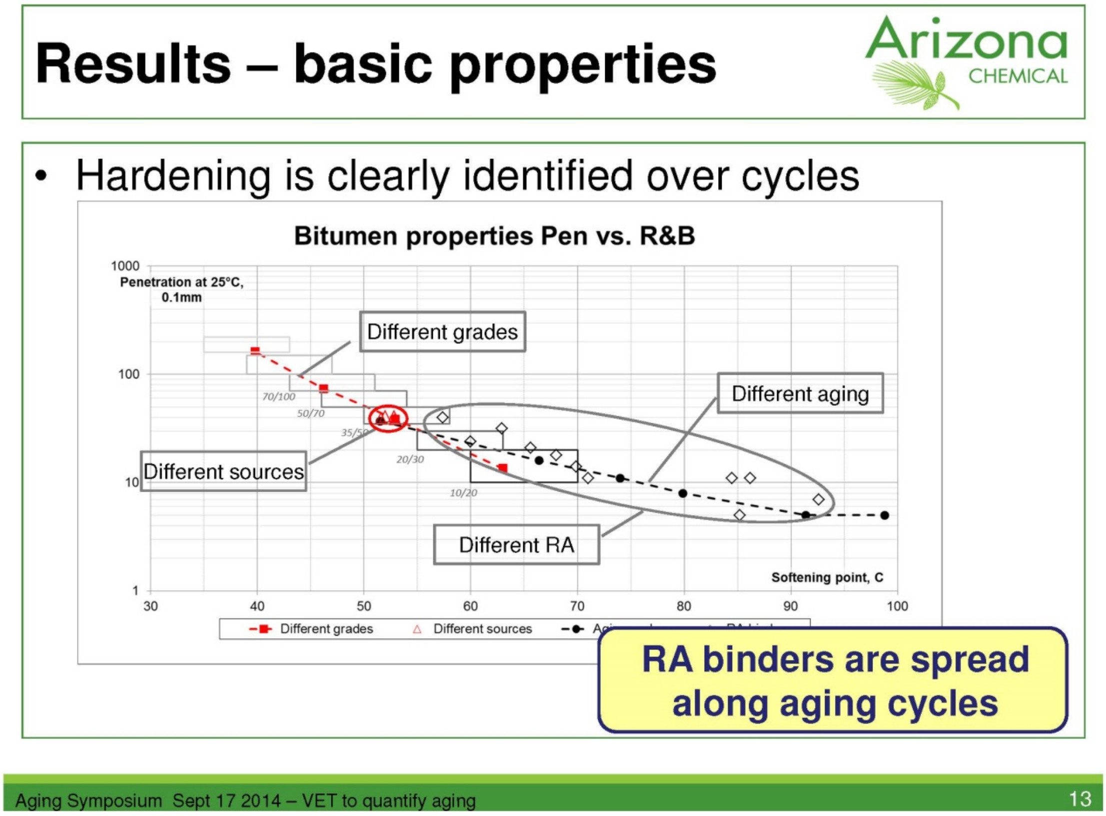
Results – basic properties
Arizona
CHEMICAL
• Hardening is clearly identified over cycles
Bitumen properties Pen vs. R&B
Penetration at 25°C, 0.1mm
1000
100
10
1
30
40
50
60
70
80
90
100
Softening point, C
70/100
50/70
35/50
20/30
10/20
Different grades
Different aging
Different sources
Different RA
Different grades
Different sources
RA binders are spread along aging cycles
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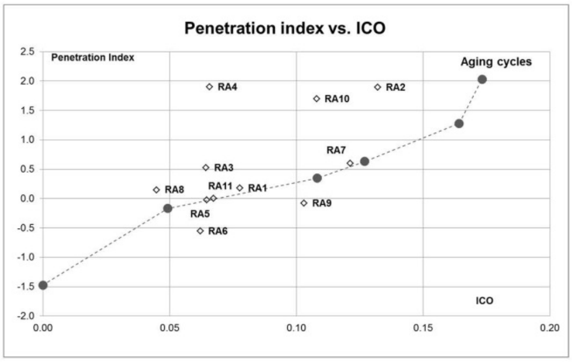
13

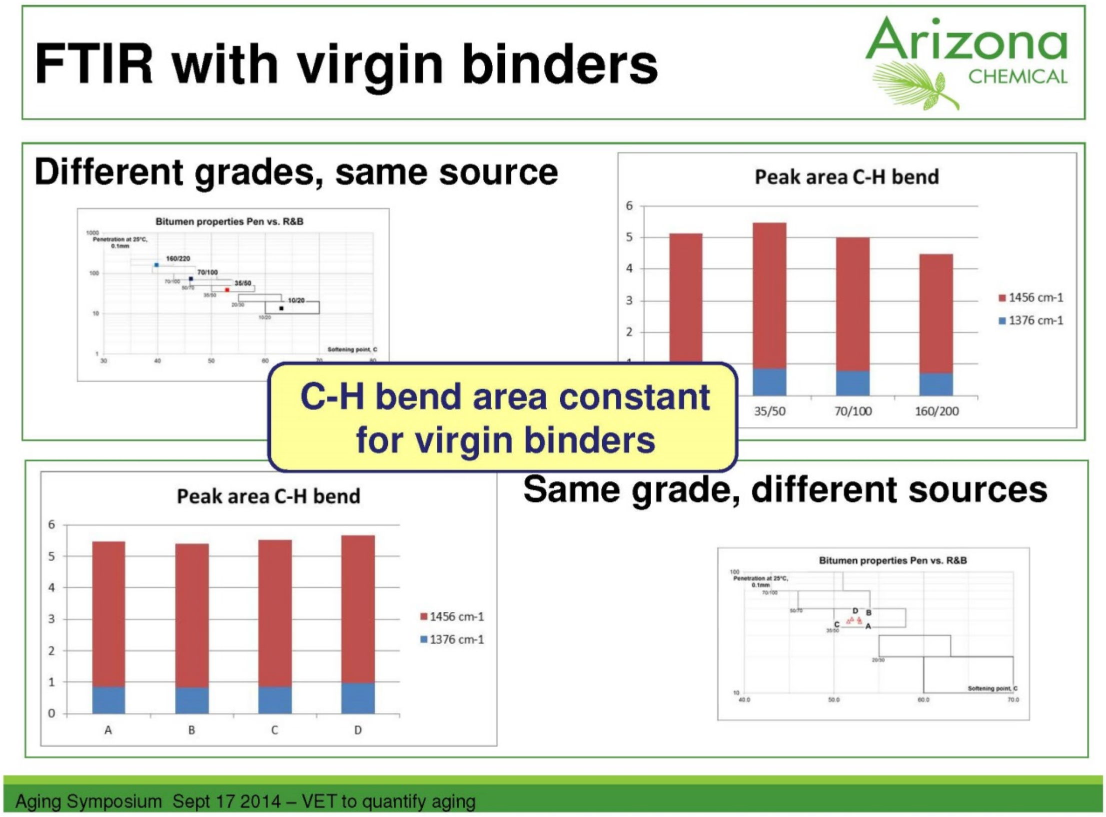
Simple analysis

Arizona CHEMICAL

- Penetration Index considered as indicator of oxidation
  - With aging cycles PI increases
  - But PI trend is not obvious compared to ICO

Something more to address aging




FTIR with virgin binders
Arizona CHEMICAL
Different grades, same source
Bitumen properties Pen vs. R&B
160/220
70/100
35/50
10/20
Peak area C-H bend
35/50
70/100
160/200
1456 cm-1
1376 cm-1
C-H bend area constant for virgin binders
Peak area C-H bend
A
B
C
D
1456 cm-1
1376 cm-1
Same grade, different sources
Bitumen properties Pen vs. R&B
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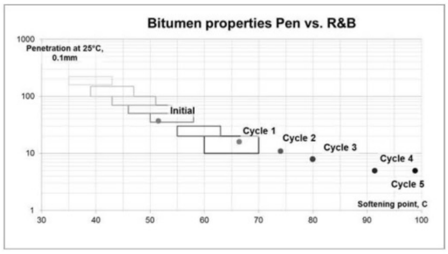
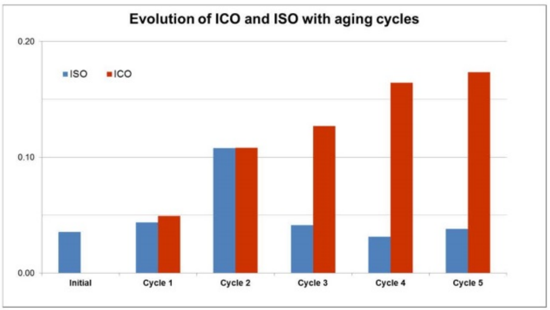
FTIR with aging cycles

Arizona CHEMICAL

- FTIR data computed for ICO and ISO index
  - ICO increases constantly over aging





Both ICO and ISO are measures of aging

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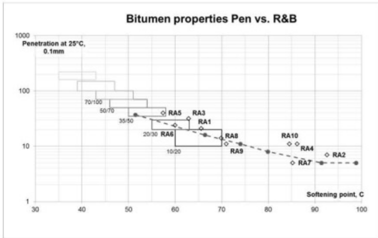
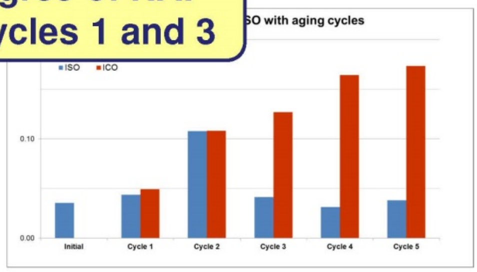
FTIR with RAP binders

Arizona CHEMICAL

- Different samples from road
  - Different locations, aging levels
  - Unknown initial grades or sources
  - ICO & ISO are in a similar range for all the RA binders



Ageing degree of RAP between cycles 1 and 3



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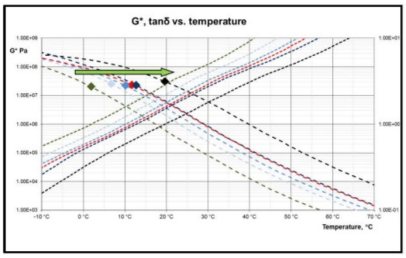
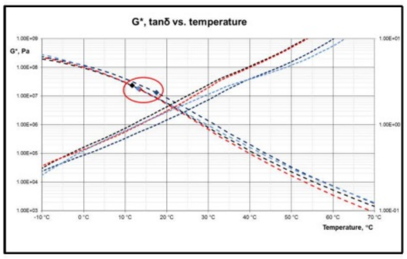
VET for virgin binder

Arizona CHEMICAL

Different grades, same source

- Shift in X-over temperature in range of 0 to 20°C
- X-over modulus almost constant above 10^7 Pa





Same grade, different sources

- Similar DSR profile
- X-over parameters close together

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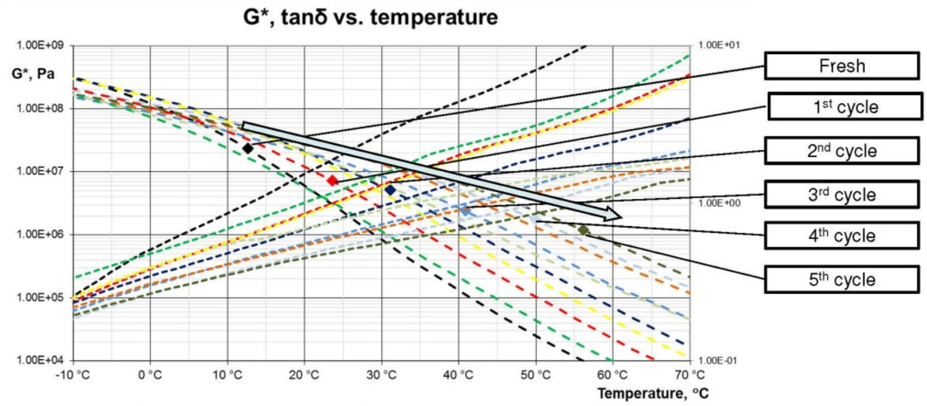
VET for aging cycles

Arizona CHEMICAL



- Increase in cross-over temperature as a result of hardening (same as with different grades)
- Decrease in G* after each cycle from temperature susceptibility

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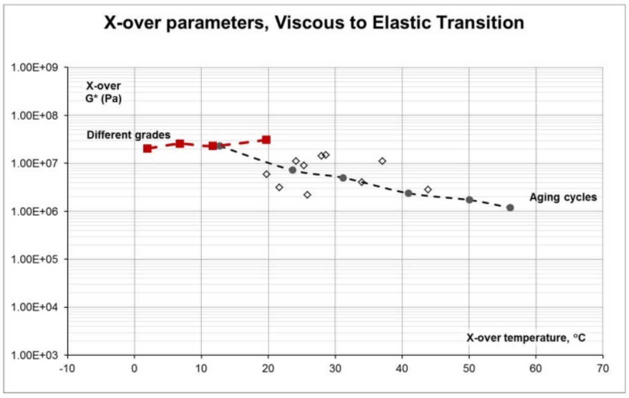
VET for with RA binders

Arizona CHEMICAL

- Different grades
  - Shift in X-over T
- Aging cycles
  - Shift in X-over T (hardening effect)
  - Shift in X-over G*

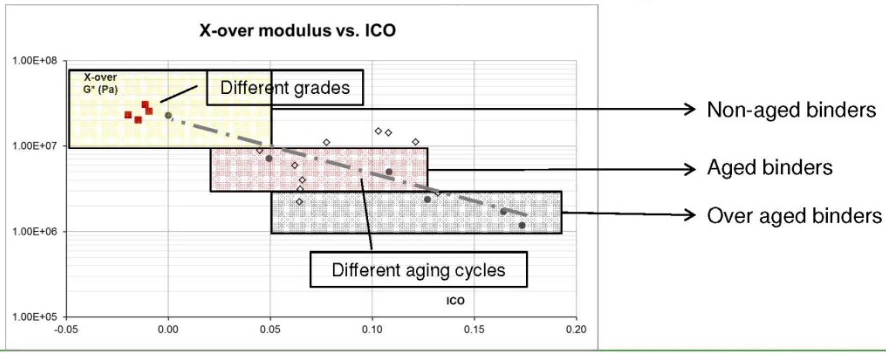


- Aged binders from road
  - Spread along the aging / grading line

X-over G* vs Carbonyl Index

Arizona CHEMICAL

- Non-aged binders are clearly concentrated with Carbonyl Index at 0
- Aging (oxidation) increases carbonyl index and decreases X-over G*
- Possible to estimate the degree of aging



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Conclusion

Conclusion

- Multi-aging extrapolates the effect of aging
- FTIR ICO relevant parameter for oxidation degree
  - Results are independent of asphalt binder grade or source
- DSR, addresses the change of mechanical behavior
  - Shear modulus alone is not enough to address aging
  - Cross over parameters are good indicators
    - Cross over temperature addressing stiffness with grading
    - Cross-over modulus addressing temperature susceptibility
- DSR and FTIR, a reasonable trend
  - A new approach to qualify the degree of aging

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Questions?

Arizona CHEMICAL

Materials

Arizona CHEMICAL

- Different asphalt binder grades

Grade	10/20	35/50	70/100	160/220
Penetration at 25°C	14	39	74	162
Softening point	63.0	52.9	50.4	39.8
Penetration Index	-1.00	-1.06	-1.29	-1.04

- Different asphalt binder sources

Source	A	B	C	D
Penetration at 25°C	39	41	39	41
Softening point	52.9	52.8	51.6	52.0
Penetration Index	-1.06	-0.97	-1.35	-1.15

- Different asphalt binder aging levels
  - A pen grade 40/60 aged through 5 cycles
- Different asphalt binder as recovered from the road
  - Various locations, unknown initial source, grade, aging

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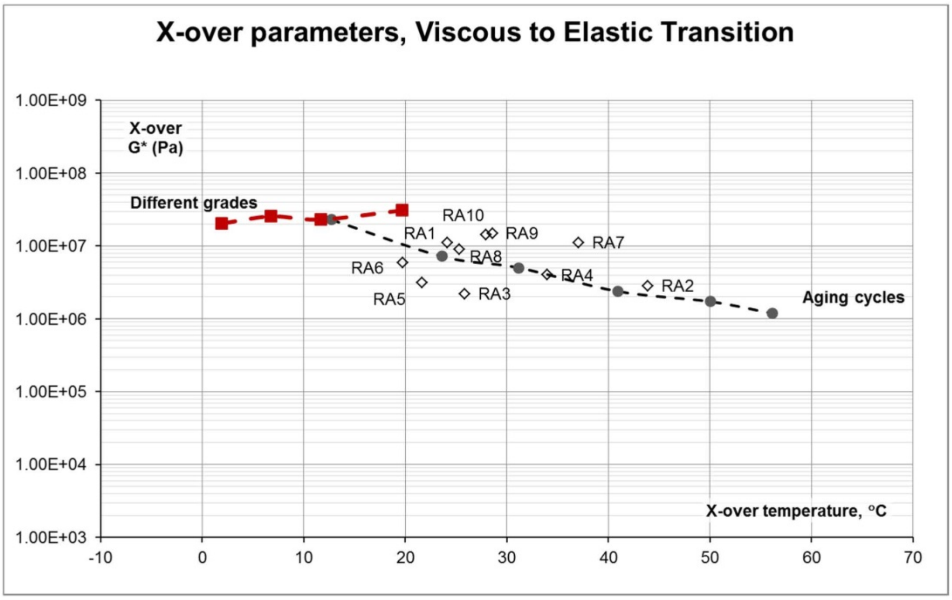
Viscous to Elastic Transition



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8.6 Markus Oeser, TU Aachen, TBA

Prevention of Asphalt Binder Oxidation using MMT-Particles

Markus Oeser
RWTH Aachen University
Uwe Beginn
UNI Osnabrück

Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

FE 07.0243/LRW/2011

„NANOASPHALT – Optimization of the Performance Characteristics and the Durability of Asphalt Pavements using Nano-Technology"

Diesem Vortrag liegen Teile des im Auftrag des Bundesministeriums für Verkehr und digitale Infrastruktur, vertreten durch die Bundesanstalt für Straßenwesen, unter FE 07.0243/2011/LRB laufenden Forschungsvorhabens zugrunde.

Die Verantwortung für den Inhalt liegt allein beim Autor.

The presentation is based on parts of the research project carried out at the request of the Federal Ministry of Transport and Digital Infrastructure, requested by the Federal Highway Research Institute, under research project No. 07.0243/2011/LRB.

The author is solely responsible for the content.

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

Challenges in Asphalt Pavement Engineering

- Increasing Axle Loads
- Climate Change
- Changing Quality of Resources
- Fewer Resources
- Workability
- Work Safety
- Environment Protection
- Energy Efficiency

etc.

3

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Prevention of Asphalt Binder Oxidation using MMT-Particles

Improving the Performance of Bitumen through Modification

- Polymer Modification
- Rubber Modification
- Wax Modification
- Primer
- Nano Modification

4

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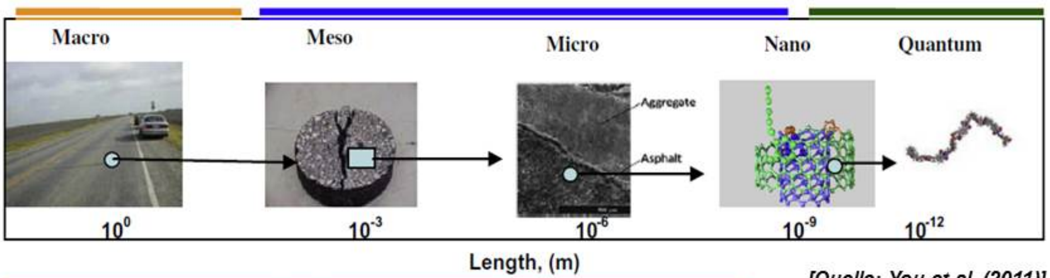
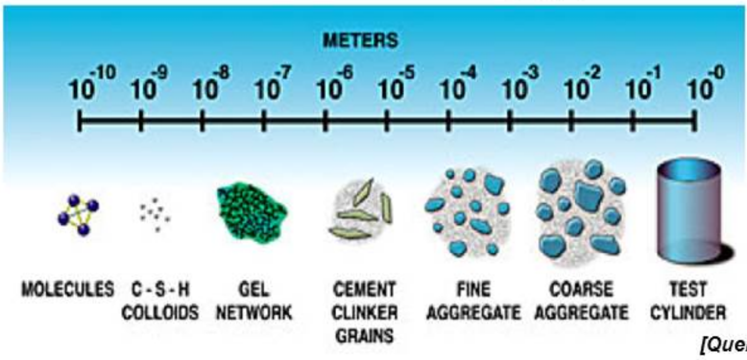
Prevention of Asphalt Binder Oxidation using MMT-Particles

Length Scales



[Quelle: You et al. (2011)]



Length of light waves
380 nm to 780 nm

[Quelle: Resperion Whitepaper (2008)]

5

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Prevention of Asphalt Binder Oxidation using MMT-Particles

Asphalt Performance Optimization using Nano-Technology

a) Bound between grains

b) Mastics (Stiffness, Cohesion etc.)

c) Bound between the layers

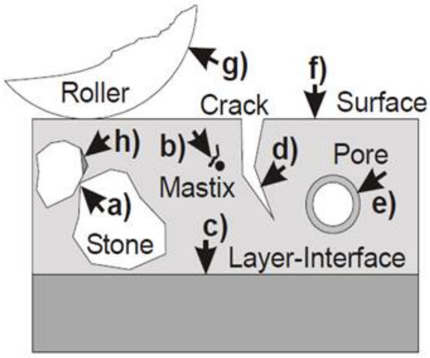
d) Crack healing

e) Binder Oxidation

f) Surface Characteristics

g) Adhesion / Anti-Adhesion Characteristics

h) Grain-Mastics-Adhesion



Source: Partl et al., 2004

6

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Prevention of Asphalt Binder Oxidation using MMT-Particles

Approach

Basic Idea:

- Adding (MMT-Nano-Particles (Montmorillonite) to asphalt bitumen
- Guaranteeing for an exfoliated alignment of the particles

Result:

- Reducing the susceptibility of asphalt bitumen to aging
- Increasing the barrier characteristics of asphalt binder

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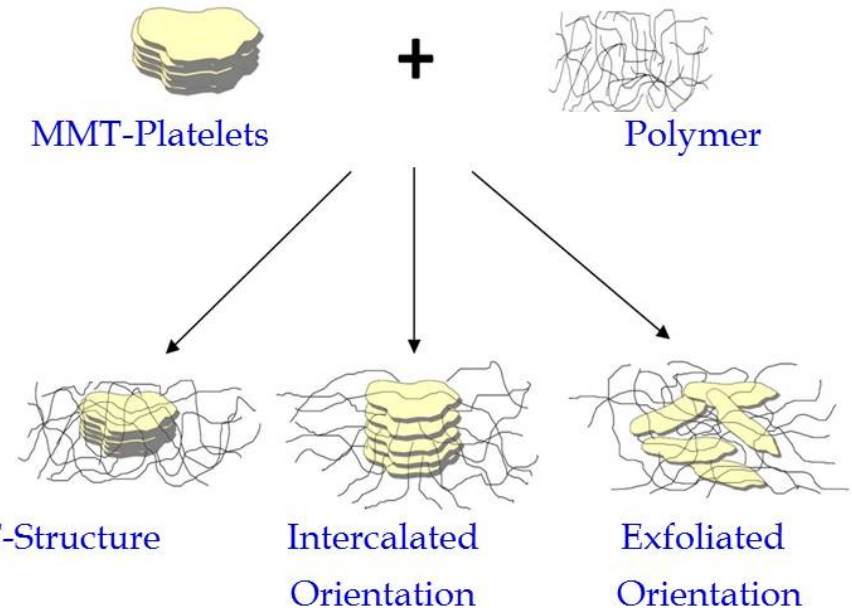
Prevention of Asphalt Binder Oxidation using MMT-Particles

Alignment / Orientation



8

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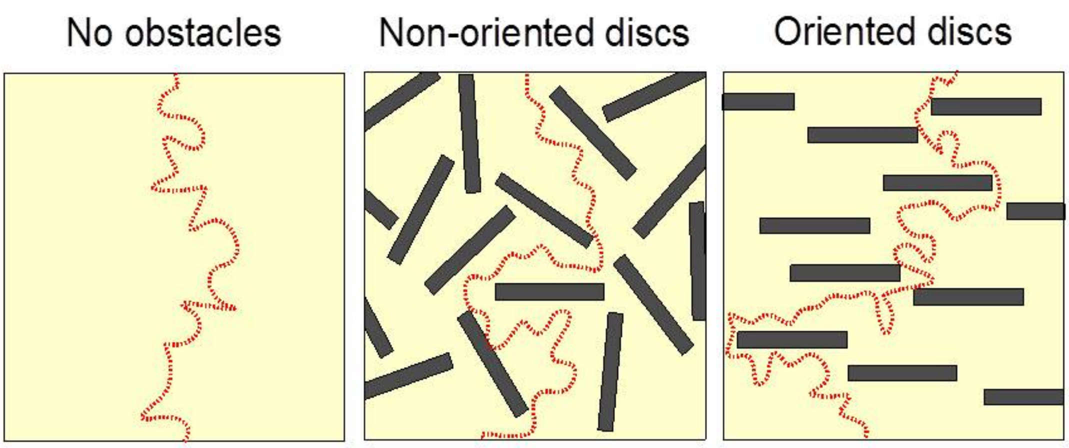
Prevention of Asphalt Binder Oxidation using MMT-Particles

Principle: Reducing the Diffusivity of Asphalt Binder



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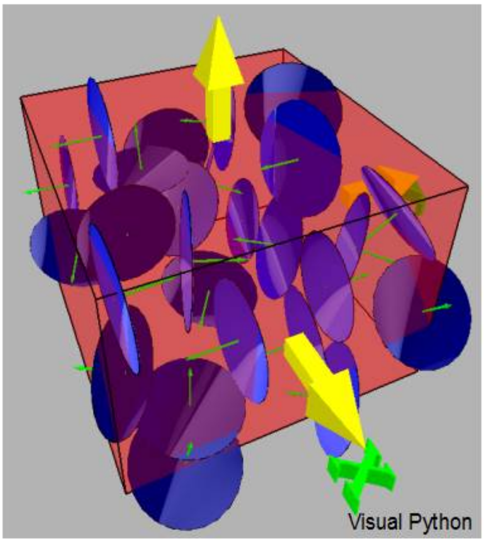
Prevention of Asphalt Binder Oxidation using MMT-Particles

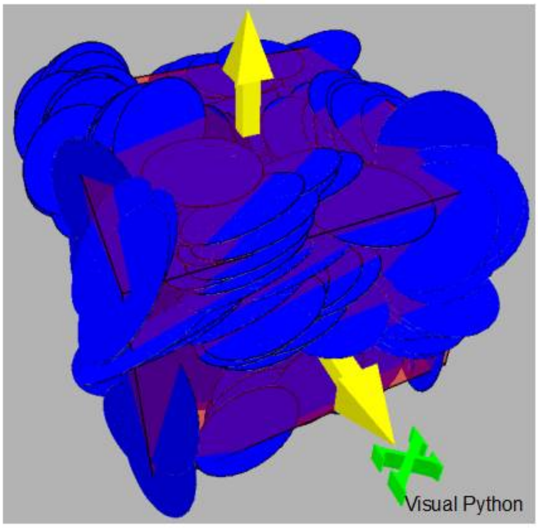
Principle: Reducing the Diffusivity of Asphalt Binder

$R_D = 1.00, H_D = 0.01$



$\Phi_D = 0.005, N_{DSC} = 27$

$R_D = 1.00, H_D = 0.01$



$\Phi_D = 0.050, N_{DSC} = 326$

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Prevention of Asphalt Binder Oxidation using MMT-Particles

Laboratory Shear Mixer L5M

Capacity
1 ml to 12 liter
Engine
250/750 W , 220 Volt, 50/60 Hz. 8000 R/min (6000 R/min in 12 liters are used).

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Sample Preparation

Nano-composite MMT

Breaking the MMT composite

Shear Mixer

Adding MMT

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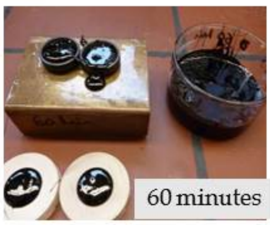
Prevention of Asphalt Binder Oxidation using MMT-Particles

Test program (Trials)

- Variants
  - Bitumen 50/70 with 5 M.-% MMT
  - PmB 25/55-55 A with 5 M.-% MMT
- Tests
  - Mixing time: 0, 5, 10, 20, 30 and 60 minutes
  - Characterization: Pen, Softening Point, DSR
  - Visual inspection/observation (Agglomerates? ⇨ **N E I N** <u>but</u> little air bubbles)



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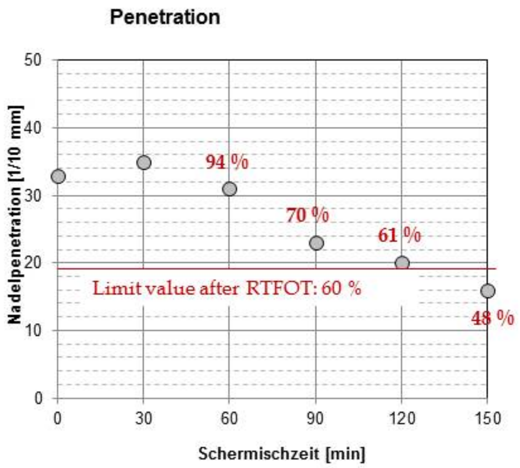
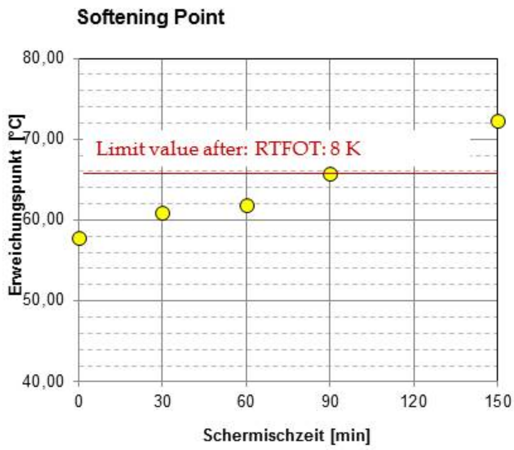
Influence of the Mixing Duration

- Bitumen: PmB 25/55-55 A
- Mixing Parameters: N = 5.000 U/min, T = 160 °C, ohne MMT





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Prevention of Asphalt Binder Oxidation using MMT-Particles

Prüfungen an Nanopartikel-Bitumen-Kompositen (NPBK)

- Materials:
  - Bitumen: PmB 25/55-55 A
  - Nano Particles: Montmorillonite (MMT)
- Tests:
  - Needle Penetration
  - Softening Point
  - DSR-Analytic

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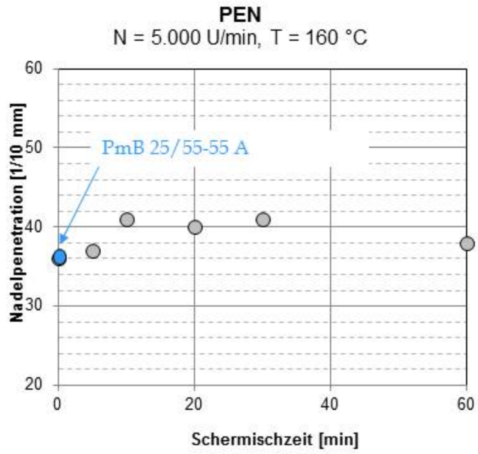
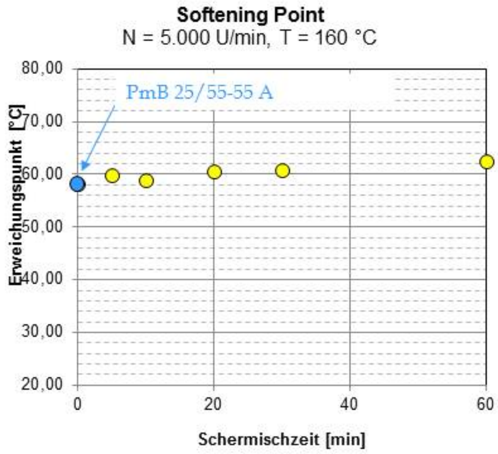
Results: PmB 25/55-55 A with 5 M.-% MMT





- Small reduction in penetration after MMT has been added
- Almost no influence of the Softening Point

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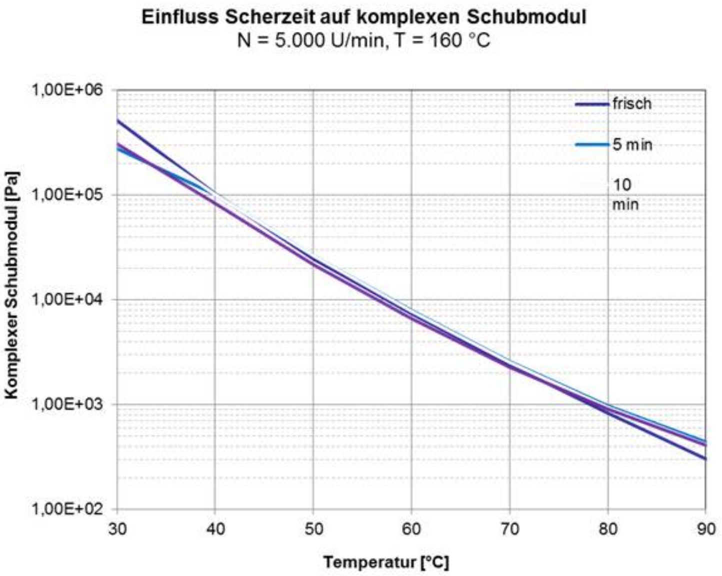
Prevention of Asphalt Binder Oxidation using MMT-Particles

Results: PmB 25/55-55 A with 5 M.-% MMT



- No significant changes

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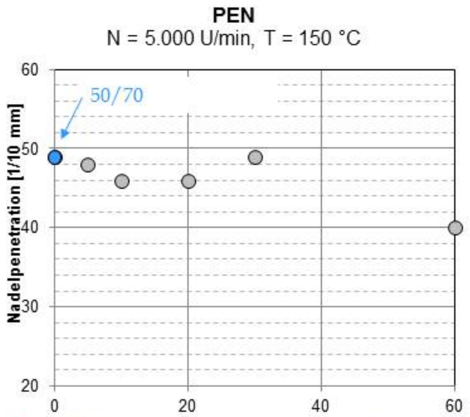
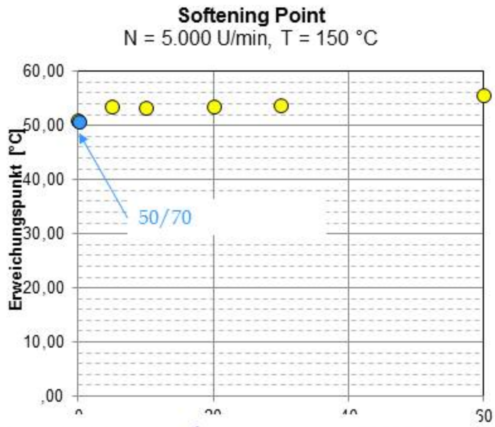
Prevention of Asphalt Binder Oxidation using MMT-Particles

Results: 50/70 with 5 M.-% MMT





- If the mixing time is less than 30 minutes, changes in PEN and Softening Point can be attributed to the MMT particles added!
- If mixing time exceeds 30 minutes , bitumen becomes significantly harder.

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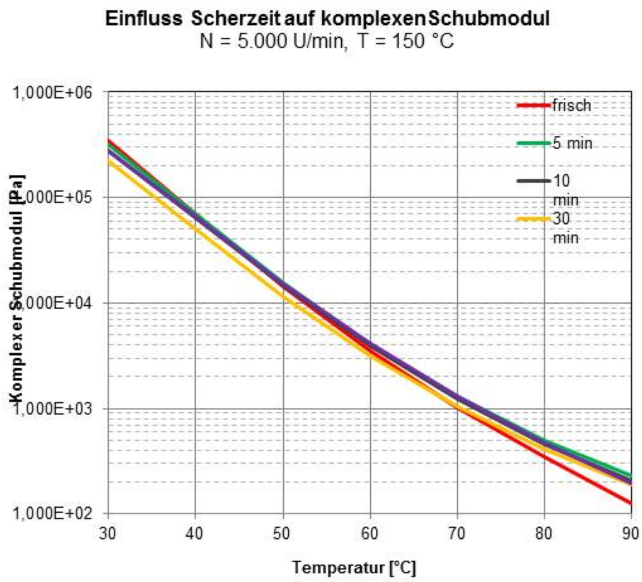
Prevention of Asphalt Binder Oxidation using MMT-Particles

Results: 50/70 with 5 M.-% MMT



- No significant changes
- Slightly higher module at very high temperatures

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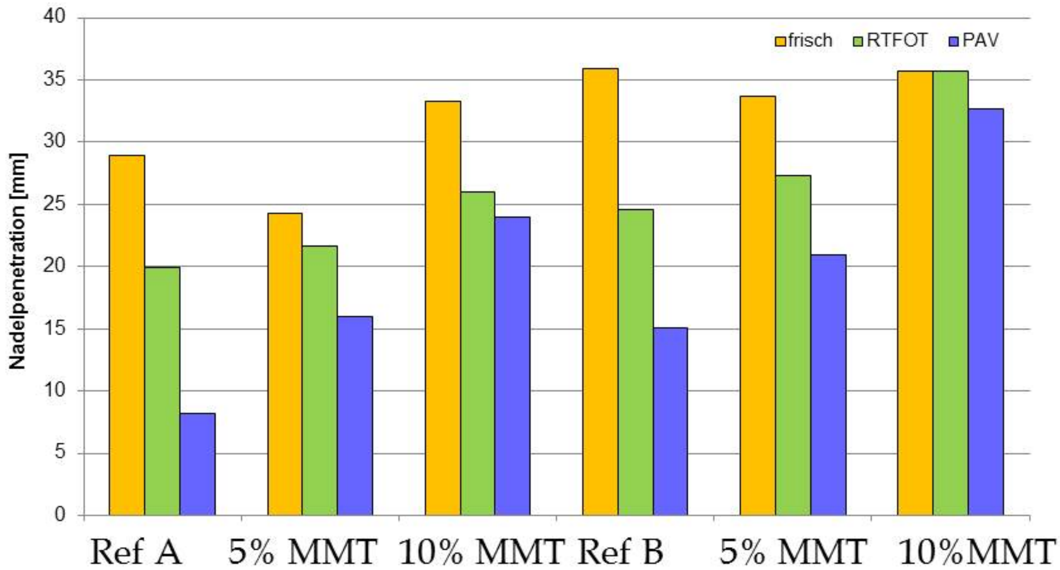
PEN



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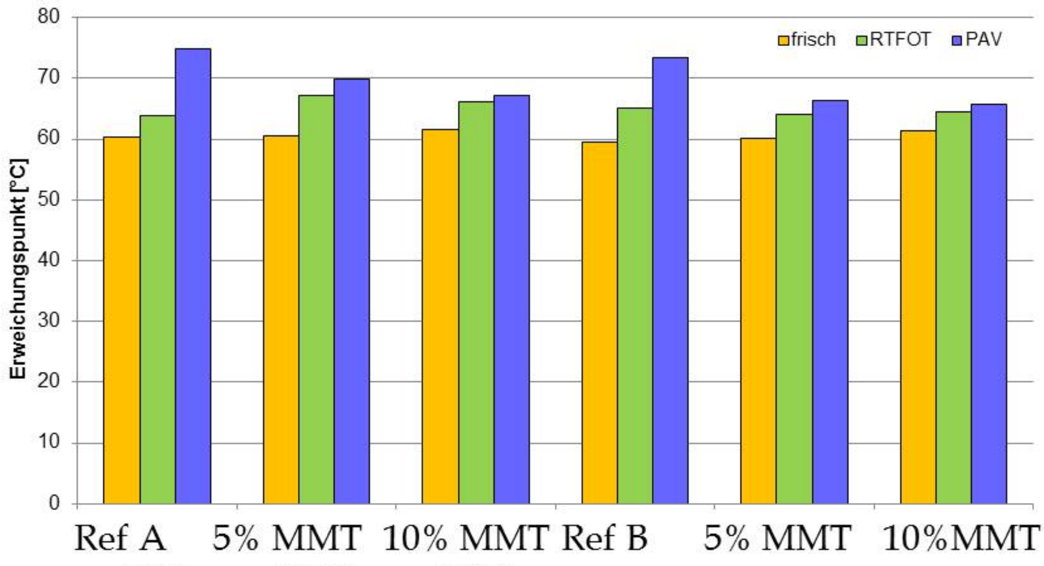
Softening Point



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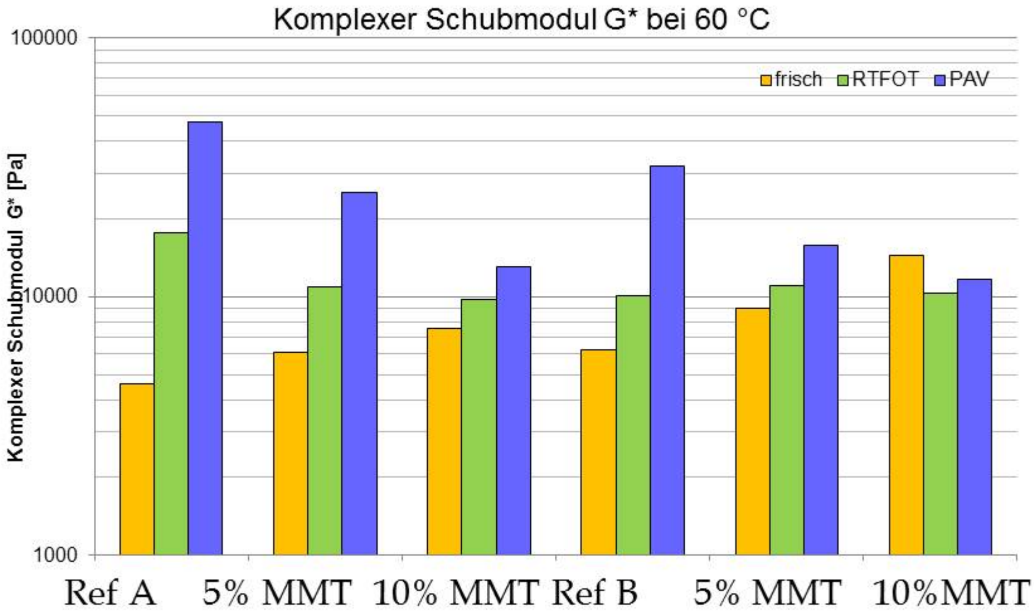
DSR-Results



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Prevention of Asphalt Binder Oxidation using MMT-Particles

Conclusions

- MMT particles can be easily mixed in the binder using a simple shear mixed.
- Even after a mixing time of only 5 minutes (at N = 5.000 R/min) sample appears homogeneous. Dark field microscopy will be carried out to gain further information!
- Influence on PEN and Softening Point is quite low.

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Prevention of Asphalt Binder Oxidation using MMT-Particles

Conclusions

- Production of larger quantities of MMT-modified bitumen appears to be feasible.
- Technique needs to be up-scaled to be used in mixing plants.
- Rate of oxidation is reduced
- Influence on the adhesion between the grains and the mastics is to be investigated.
- Influence on the cohesion of the bitumen will be studied in future.
- Asphalt tests will be done.

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Prevention of Asphalt Binder Oxidation using MMT-Particles

The End!

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