Study on the ageing behavior of South American bitumen

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Abstract In Suriname, located at the north east part of South America, only one type of bitumen is available for road construction. This bitumen, a pen grade bitumen 60/70 is produced by the Surinam refinery Staatsolie. The crude is always of the same origin. Based on the climatic conditions, it is presumed that ageing of bitumen is often the cause of premature damage in different types of roads, such as fatigue and alligator cracks, raveling and potholes. To obtain insight to which extent the ageing behavior of the bitumen provides an explanation for the premature failure, extensive research has been conducted on bitumen recovered from three premature damaged road sections.
The degree of short term ageing was first examined by means of empirical bitumen test methods, rheological characterization, FTIR analysis and GPC measurements. After this an attempt was made to mimic the observed long term field ageing using the RCAT method. This paper reports on the research carried out on field aged and RCAT artificially aged bitumen and the relationship between field and artificially aged bitumen.

Keywords Bitumen, Ageing, RCAT, FTIR, GPC

1 Introduction

1.1 General

Due to exposure of oxygen, UV and high temperatures bitumen undergoes changes during its service life which finally results in a decrease of its functionality. When applied in asphalt mixtures, aged bitumen results in a loss of mixture properties which on its turn enhances the initiation and propagation of damage in asphalt pavements. It is widely reported and accepted in pavement engineering that a proper mixture design and material selection procedures are of paramount importance for obtaining the maximum performance in practice. Here maximum performance is described by the optimum between durable, sustainable and economic benefits. Especially for pavement engineers the challenge lies in assuming an technical lifetime expectancy for asphalt mixtures in e.g. maintenance schemes.

The latter requires accurate information about the long term field behavior of different asphalt mixtures. In the quest for predicting this long term field performance, numerous studies (van Oort 1954, Petersen et al. 1994, Hagos 2008, Das 2014) have been conducted during the past 65 years all over the world. Majority of these studies focusses on understanding the phenomena that occur and develop in bitumen during its service life. The authors believe that it is of little use to summarize concluding results from previous studies. Instead they believe that implementation of these findings in daily practice, identification of practical issues towards the implementation and development of practical decision tools provides a more solid base to assist pavement engineers towards making choices. Subsequently these practical "unknowns" can provide new insights when setting up an experimental plan for laboratory experiments which is what this paper focusses on.

1.2 Ageing of bitumen in general

Bitumen, sometimes referred to as the "left overs" of straight run distillation process, is an organic material from which the exact composition is not yet known (Read & Whiteoak 2003), because of its complexity. As a result, capturing all the compositional changes that occur due to ageing and relating these changes to physical properties are considered to be more spot measurements which help to understand but cannot be simply extrapolated to develop a general explanation.

Traditionally regarded as a colloidal system, bitumen consists of highly polar and high molecular weight asphaltene micelles which are hosted in a lower molecular weight oily medium, usually referred to as maltenes. Maltenes can be divided into saturates, resins and aromatics. The overall proportions in which the different molecules are present in the bitumen, determines its overall behavior (Read & Whiteoak 2003).

Being an organic substance the mechanical properties and the chemical structure of bitumen can deteriorate due to exposure to the environment which is also known as age hardening. This ageing of bitumen is considered to be mainly caused by the oxidation and ultraviolet (UV) radiation. In this process, temperature plays the role of a catalyst. Oxidative surface ageing is an irreversible chemical reaction between hydrocarbons of bitumen and available atmospheric oxygen. The UV radiation catalyzed reaction occurs rapidly, which takes place at the few top millimeters of the exposed bitumen surface (Hagos 2008, Petersen 2009). During both processes several carbon groups are formed which increase the polarity of the host compounds and make them much more likely to associate with other polar compounds. As they form these associations, they create less soluble hydrocarbons which in turn increase the bitumen's viscosity (Lesueur 2009, Redelius 2009) and affect other physical properties.

The above mentioned chemical and/or compositional changes occur rapidly during the mixing and laying process of the asphalt mixture (short term ageing). On the road the ageing occurs at a much slower rate (long term ageing). Several studies (Petersen et al. 1994, Hagos 2004, Das 2014) have tried to capture these changes and develop laboratory ageing protocols to mimic the field ageing.

Majority of these protocols are performed using laboratory ageing methods and to speed up the research time relative high temperatures are used, which doesn't occur in the actual pavements in practice. Further on in most situations, the initial mechanical and chemical properties of the bitumen used in the pavement was not measured, one type of bitumen produced from different crudes is used, actual loading on the pavement is not always monitored while in some situations, high temperature periods can heal damage which is initiated during winter periods.

As a result, correlating observed damage in practice to changes in bitumen properties, consist of relative large uncertainties.

1.3 Objectives

In Suriname, located on north east coast of South America, the bitumen used in road construction is supplied by the state-run company Staatsolie. Suriname's land area is part of the Guianas Shield that runs from Venezuela to French Guiana and could contain recoverable oil reserves over 13.6 billion barrels and gas reserves of 39 trillion ft3 (Argus 2014) estimated by the US Geological Survey. It is interesting to note that in road construction only one type of bitumen is used for the different asphalt layers (NEA 2010) while the crude is constant making it thus interesting and obviously less complex, to investigate variation of the bitumen properties in time and its effect on pavement performance. This is important, because Suriname has a tropical climate, the average high respectively low temperatures are 32 and 23°C, the UV index is between 10 and 11.

Despite the above, little to no attention is paid to the engineering properties of the bitumen and it's possible variations on pavement performance in practice. The reasons behind this were captured in an EU funded project called "Institutional Strengthening of the Transport Sector" (ISTS) in Suriname which ran from 2009 – 2011 (NEA 2010). The results of the project motivated the quest to develop a practical framework for the Suriname Ministry of Public Works and local contractors in order to improve and optimize current maintenance strategies.

The main objective of this study was to characterize the bitumen from Suriname using test methods which are commonly adapted when studying the ageing of bitumen. The characterization was performed on virgin bitumen and artificially aged bitumen and then compared with field obtained samples. Observations from the different phases are discussed, providing a useful starting point and criteria for road authorities and contractors towards the implementation of quality control indicators for bitumen deliveries in practice and the monitoring of long term field behavior of bitumen and thus pavement performance.

2 Experimental

2.1 Materials

The bitumen used in this study is pen grade 60/70 bitumen produced by Staatsolie. The properties of the bitumen are summarized in table 1.

Table 1 Properties virgin pen grade 60/70 bitumen

API gravity (-)	8,8
Penetration 10^{-1}mm(T= 25°C)	63
Softening point R&B (°C)	47,2

Apart from investigating virgin bitumen, bitumen was recovered from field samples, cored in 2013 from three different locations. Cores were taken from the surface layer and the binder layer, which failed prematurely. At all three locations, a dense asphalt concrete mixture was applied for both layers. For location C, bitumen was recovered only from the binder layer. Table 2 describes the different field samples.

Table 2 Properties field samples

Sample id	Location (layer)	Thickness (mm)	Age (years)
A1	A (surface)	33	5
B1	B (surface)	45	11
C2	C (binder)	50	4

The recovery of the bitumen from drilled field cores was performed on the total core itself. No distinction was made between the upper part and the bottom part of the asphalt layer. The reasons for this were some local practical constraints such as too less available cores. Knowing that ageing in practice differs as function of asphalt layer thickness, in this study it was decided to continue with the recovered bitumens from the whole cores while at the same time highlighting the importance for proper preparation of test samples.

Visual inspections at the different sites revealed that the observed failure was more local, structural failure which suggested that bitumen ageing and its impact on mixture performance might not have been the primary cause for the manifested damage. This observation stipulates the difficulty when developing models to predict long term pavement performance on the basis of ageing studies on bitumen level. Apart from defining a preferred asphalt mixture property which varies from country to country, the authors believe that it is equally important to characterize bitumen using test methods which correlate or can easily predict mixture performance.

Fig. 1 Observed damage: (left) location A, (middle) location B, (right) location C

2.2 Test methods

All the studied bitumens were subjected to physical and chemical characterization. Empirically, the bitumens were subjected to softening point measurements according to the European standard EN 1427.

Complex modulus and complex viscosity measurements were carried out using an Anton Paar MCR302 rheometer. Complex viscosity measurements were performed using the cone-plate (D=25mm) setup at an incremental shear rate from 0.1 – 300 (1/s) at two temperatures, 100°C and 135°C.

Frequency sweeps were performed using the plate-plate setup in a temperature range from -10°C to 50°C and frequency range from 0.1 to 300 rad/s. To construct a mastercurve, the different isotherms were shifted using the William Landel Ferry equation (Christensen 1982), Eq.1, while for quantitative comparison purposes, a model was fitted in the shifted test results. The model used was a modified Huet – Sayegh (Huet 1963), developed by Woldekidan (Woldekidan 2011), Eq. 2.

$$\log(a_T) = \frac{-C_1(T-T_r)}{C_2+(T-T_r)} \quad (1)$$

$$(G^*(\omega))^{-1} = (G_0 + \frac{G_\infty - G_0}{1+\delta(\mathrm{j}\omega\tau)^{-m_1}+(\mathrm{j}\omega\tau)^{-m_2}})^{-1} - \frac{\mathrm{j}}{\eta_3\omega} \quad (2)$$

In Eq. 2, $G^*(\omega)$, G_0 and G_∞ denote the complex shear modulus, rubbery shear modulus, here assumed to nil, and the instantaneous shear modulus value. The model parameters δ, ,$m_1$and m_2 are identical as the original Huet – Sayegh model while the terms τ and η_3 denote the time constant and the linear dashpot parameter.

The addition of a linear dashpot element in series with the original Huet – Sayegh model, makes the model attractive for modelling the permanent deformation of asphalt mixtures. In Suriname usually bitumen rich mixtures, such as dense asphalt concrete, are applied as surface layers. In these mixtures the contribution of the viscous deformation of the bitumen to the overall mixture deformation is significant. Since the bitumen type and crude are constant, the model parameters can serve as an excellent measure to optimize rutting properties of asphalt mixtures. Subsequently modelparameters can also serve as quality control indicators.

To investigate the chemical changes due to environmental conditions and artificially ageing, Gel Permeation Chromatography (GPC) and Fourier Transform Infrared (FTIR) spectroscopy measurements were carried out.

Artificially long term ageing of the virgin binder in the laboratory was conducted using the Rotating Cylindrical Ageing Test (RCAT). Due to practical limitations, the short term ageing (RCAT 163) was not performed. The bitumen was subjected to a temperature of 90 °C with a constant flow of oxygen. Conditioning and oxygen rate were selected according to European standard EN 15323. Samples for further analysis were taken after the following time intervals: 4 hours, 21 hours, 48 hours, 144 hours and 240 hours.

3 Results & Discussion

3.1 Empirical

Figure 2 presents the measured softening points of the different bitumens. All the field binders show an increased softening point. A difference of approximately 6°C is observed between the virgin and field bitumens. For the C2 bitumen which was recovered from the binder layer, an increase of 2°C was measured. Because the service life of B1 is 11 years, a higher softening point is expected than A1, which has a service life of 5 years. Possibly the short term ageing caused by production, transport and laying may differ, but this is unknown. The results suggest that to mimic 5 to 11 year field ageing of the bitumen of the top layer, it takes about 21 hour artificial ageing with RCAT to obtain identical softening points while for the binder layer, it takes less than 4 hours.

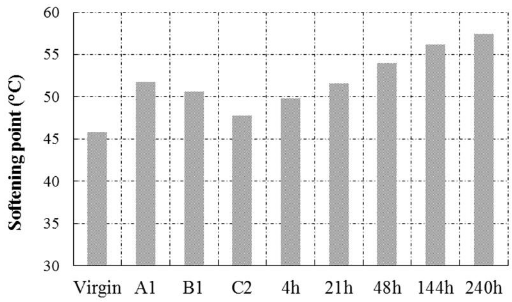

Fig. 2 Softening point results of virgin, field and artificially (RCAT) aged bitumen

3.2 Rheological

Table 3 summarizes the obtained model parameters for the different bitumens. Using the model, the complex modulus was calculated at two different loading frequencies. The behavior of the different binders at these frequencies is compared in figure 3.

Table 3 Obtained model parameters, $T_{reference}$ = 30°C

Par.	C_1	C_2	m_1	m_2	δ	τ (s)	η_3 (MPa.s)	G_∞ (MPa)	r² G*	r² Phase
Virgin	14,8	139,3	0,17	0,53	0,10	5,12E-02	0,05	930	0,999	0,999
A1	14,4	144,9	0,21	0,57	5,02	1,63E-01	0,16	1000	0,998	0,996
B1	15,0	148,0	0,30	0,69	4,93	1,28E-01	0,13	532	0.999	0,997
C2	16,1	160,5	0,23	0,61	4,66	8,01E-02	0,08	1000	0,998	0,997
4h	11,9	115,8	0,18	0,56	2,88	8,02E-02	0,08	1000	0,994	0,996
21h	12,7	124,6	0,20	0,57	2,52	1,28E-01	0,13	710	0,998	0,996
48h	13,2	127,6	0,21	0,59	2,70	1,77E-01	0,18	719	0,988	0,996
144h	18,0	156,5	0,21	0,59	3,39	4,68E-01	0,47	927	0,999	0,998
240h	18,0	160,0	0,20	0,55	2,82	6,00E-01	0,60	772	0,999	0,997

The obtained correlation coefficients the for the complex modulus and phase angle, in the last two columns of table 3, indicate the accuracy of the model to describe the measured data within the tested range. The found differences for the model parameters indicate that due to ageing, the response of the different bitumens at a given temperature changes. This is illustrated in figure 3.

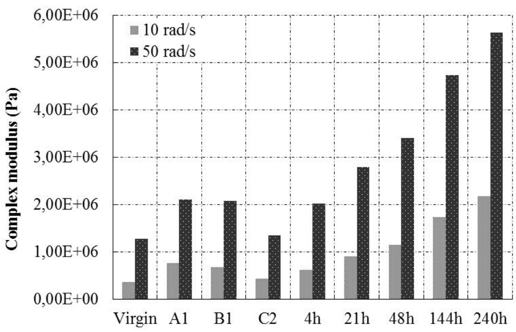

Fig. 3 Comparison of complex modulus at an reference temperature of 30°C

This change in response is best illustrated in figure 4 where the results of the complex viscosity measurements are compared with each other. All samples were subjected to an incremental shear rate from 0,1 to 300 s-1. In figure 4 the resulting shear stresses in the sample are plotted against the calculated viscosity. All the test results follow the same trend while it can be observed further that the resulting shear stresses are the lowest for the virgin material and the highest for the A1 bitumen and the 240 hours artificially aged bitumen.

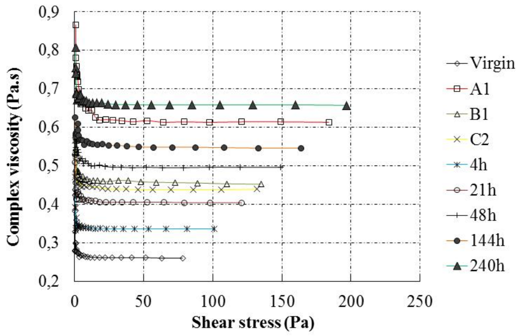

Fig. 4 Test results complex viscosity measurements at test temperature of 135°C

In figure 5 the complex viscosities of the different bitumens are compared with each by means of an ageing index. The measured viscosities for all the samples were divided by the viscosity of the virgin bitumen. Comparisons are made for viscosity values at a shear stress of 50 Pa.

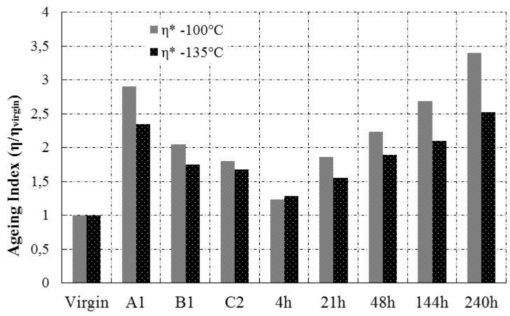

Fig. 5 Comparison of test results complex viscosity measurements

It can be seen in figure 5 that the required ageing time to mimic field measured viscosity values, ranges from approximately 21 to 240 hours. Interestingly this required time differs from the required time to obtain identical softening points and complex modulus values while the observed trend between the different bitumens remains constant in the different test methods.

3.3 Chemical

In figure 6 GPC results from the different bitumens are compared with each other. by dividing the measured data into two groups:

- Molecules with a mass greater than 4500 Dalton
- Molecules with a mass smaller than 500 Dalton

It can be observed that ageing results in an increase of the larger molecules and subsequently a decrease in smaller molecules is observed. This confirms that maltenes during the ageing process transform party to asphaltenes. It is interesting to note that for dense asphalt mixtures, ageing usually occurs at surface of the layer and in this study the bitumen was recovered from the total core. Despite this, a clear change in molecular mass is observed even for bitumen C2, recovered from the binder layer.

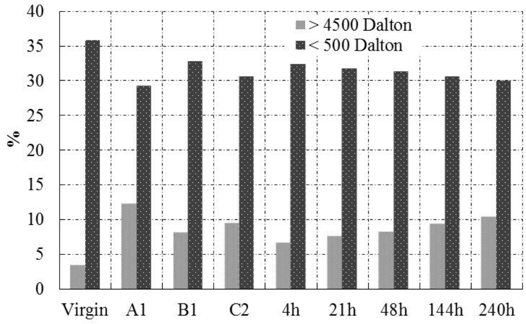

Fig. 6 GPC test results

In figure 7 a comparison is made between the different bitumens by means of infrared measurements. The area under de peak at the intervals which indicate the formation of ageing components, was calculated by available software packages. Some scatter is observed for the artificially aged samples however a logical trend can be observed that the area under the peaks increases with ageing time. It is interesting to observe the relative large difference between the field samples and the artificially aged samples. Considering the facts that the field bitumens were recovered from the total core itself and that all these samples have experienced the production a processing phase in practice, the differences could possibly be explained by the absence of the short term ageing which was not performed in this study.

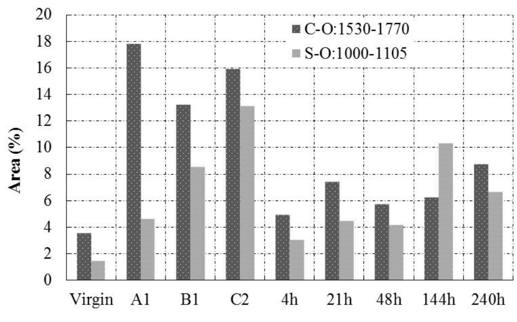

Fig. 7 Computed area under peak at different wave length intervals

3.4 Discussion

All the studied bitumens showed that ageing affects both the physical and chemical properties of the original bitumen. The difference in required ageing times to mimic field values stipulates the importance of selecting the correct initial values when one wants to calculate ageing indices. Here it was assumed that the tested virgin bitumen was identical for the field locations and storage and production conditions at the asphalt mix plant were constant hence the observed differences in required laboratory ageing time to mimic field values for the studied properties. Apart from this, bitumen was extracted from the total core itself. Nevertheless the results were discriminative enough to compare the different bitumens with each other which was also confirmed by the constant arrangement of the samples in the different test methods.
The methodology used in this study provides an excellent starting point to develop an understanding about long term pavement performance in practice. However to be able to accurately predict technical lifetime expectancies in practice on the basis of bitumen ageing rates, the authors believe it is mandatory to capture the properties of bitumen before production, after production and during its service life by means of periodically field sampling.

4 Conclusions & Recommendations

On the basis of all the obtained test results, the following conclusions and recommendations are summarized:

- To mimic long term field ageing under Surinam climate conditions, 4 to 24 hours RCAT ageing is sufficient for top layers and less than 4 hours is sufficient for binder layers.

- RCAT ageing mimics the field long term ageing, but the required time to mimic the field obtained properties differ from property to property and also differ for the recovered field bitumens.

- Recommended is to focus on the upper part of a core, when field ageing of top layers is the topic, this will give more discriminative results.

Acknowledgments The authors wish to acknowledge Dr. Wim van den Bergh (University of Antwerpen) and Dave van Vliet (TNO Delft) for accommodating some of the experiments. Special thanks go out to Eric van Oosterhout (InfraLinq) for performing all the rheological measurements.

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