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Published in:
Transportation Research Procedia

DOI:
[10.1016/j.trpro.2016.05.335](https://doi.org/10.1016/j.trpro.2016.05.335)

Published: 01/01/2016

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Blomberg, T., Makowska, M., & Pellinen, T. (2016). Laboratory Simulation of Bitumen Aging and Rejuvenation to Mimic Multiple Cycles of Reuse. In L. Rafalski, & A. Zofka (Eds.), *Transportation Research Procedia: Transport Research Arena TRA2016* (Vol. 14, pp. 694-703). (Transportation Research Procedia; Vol. 14). Elsevier Ltd.. <https://doi.org/10.1016/j.trpro.2016.05.335>

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6th Transport Research Arena April 18-21, 2016



Laboratory simulation of bitumen aging and rejuvenation to mimic multiple cycles of reuse

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Abstract

A laboratory study on bitumen aging and rejuvenation was conducted to investigate the effect of the multiple cycles of reuse on bitumen properties. The bitumen studied was unmodified conventional paving grade 70/100 pen bitumen which was aged in the laboratory, then rejuvenated with 650/900 bitumen back to 70/100 grade. Four aging-rejuvenation cycles were conducted and properties were tested after each step. The aging procedure consisted of Rolling Thin Film Oven Test (RTFOT) followed by Pressure Aging Vessel (PAV) aging at 90 °C for 20 hours. Results suggest that bitumen hardens the most during the first cycle of aging with the following cycles asserting less influence. The physical bitumen properties could be restored close to the original state. However, the balance of elastic and viscous component was altered towards a more elastic behavior in each cycle. Therefore, it is debatable whether rejuvenation with soft bitumen restores the entire range of performance for the bitumen. The changes cannot be chemically reversed in described process, although the rejuvenator allows for the restoration of some physical properties.

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Peer-review under responsibility of Road and Bridge Research Institute (IBDiM)

Keywords: Rejuvenator; aging; rejuvenation; GPC; SARA; DSR

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1. Introduction

In lieu of the availability of bitumen and its price uncertainty, the need to recycle asphalt in road construction has become essential. Therefore, an especial focus has arisen in finding ways to revive aged and hard bitumen concurrently maintaining the quality of the asphalt.

A laboratory study on bitumen aging and rejuvenation was conducted to investigate the effect of the multiple cycles of reuse on bitumen properties. The bitumen studied was unmodified conventional paving grade 70/100 pen (B80) bitumen which was aged in the laboratory, then rejuvenated with 650/900 bitumen (B800) back to 70/100 grade. Four aging-rejuvenation cycles were conducted to simulate multiple reuse of bitumen for hot-in place recycling (HIPR), discussed more by Makowska and Pellinen, (2015).

The Finnish Transport Agency (FTA) allows the hot-in place remixing method to be used only twice in a row due to concerns regarding pavement quality, as discussed in depth by Makowska and Pellinen (2015). HIPR consists of in-situ reheating of the existing pavement followed by milling, addition of the rejuvenator and fresh admixtures, followed by the homogenization of the produced layer before the final compaction.

The objective of the study was to determine the effect of the multiple recycling and rejuvenation in laboratory conditions on the bitumen chemical composition and rheological characteristics; to determine a framework for the best optimization strategies and to evaluate quality control criteria for the rejuvenation process.

2. Materials and methodology

In the aging and rejuvenation procedure, fresh B80 was first RTFO (SFS-EN-12607-1), then PAV (ASTM D6521-13) aged at 90 °C for 20 hours. This mimics short-term aging taking place during asphalt production and long-term aging on the road. After analysis, the aged product was then rejuvenated with B800 targeting a penetration of fresh B80. Four aging-rejuvenation cycles were conducted with the properties tested after each step. Table 1 gives the properties of standard B80 and B800 used in the experiment. The value of $G^* \sin \delta = 5000$ calculated from straight run bitumen is provided in Table 1, while the fatigue cracking parameter can be found in Table 5 entry A1.

Table 1. Analyses of the test bitumens B80 and B800.

	unit	B80	B800
Penetration 25 °C	0.1 mm	86	966
Penetration 15 °C	0.1 mm	na	291
Viscosity 60 °C	Pas	114	5.03
Viscosity 135 °C	mm ² /s	296	69.7
G* at 15 °C, 1.59 Hz	Pa	4 030 000	129 000
G* at 30 °C, 1.59 Hz	Pa	263 000	7 350
G* at 60 °C, 1.59 Hz	Pa	1490	70
Calculated penetration	0,1 mm	90	881
δ at 30 °C, 1.59 Hz	°	69.7	80.9
$G^*/\sin\delta = 1 \text{ kPa}$	°C	64	42
$G^*\sin \delta = 5000 \text{ kPa}$	°C	(14)	(2)
Mass change	%	0,02	-0.17
Penetration 25 °C	0,1 mm	45	965
Viscosity 60 °C	Pas	479	8.45
Retained penetration	%	52	
Viscosity ratio		4.2	1.7

After RTFOT

The aged samples were designated as A1, A2, A3, A4, while the rejuvenated samples were R1, R2, R3 and R4, according to the cycles they have gone through. All the aging - rejuvenation cycles were performed in the same manner. However, the amount of bitumen going through each aging and rejuvenation cycle was different, due to material losses in RTFO, PAV and testing. The most material-consuming step was the RTFO as bottles could not be fully emptied. For example, for sample A1 the amount of material before and after RTFO stage was 840 g and 415 g, respectively. The rejuvenation was conducted by adding soft bitumen to the aged binder at 145 °C and mixing the blend with a stirrer for 30 minutes. The last rejuvenation had to be manually mixed due to the very small amount of material left after aging.

Typically for the purpose of rejuvenation, Penetration (Pen) value must be obtained in order to use the blending equation Eq. (1) or blending chart provided in PANK (2000),

$$Pen_{blend} = 10^{\frac{a \log(Pen_{aged}) + b \log(Pen_{rejuv})}{100}} \quad (1)$$

where Pen_{blend} – Penetration of bitumen blend after rejuvenation
 Pen_{aged} – Penetration of aged bitumen
 Pen_{rejuv} – Penetration of rejuvenator
 a and b - mass percentage of aged binder and rejuvenator, respectively.

Penetration testing requires a large portion of material (100 g), which typically corresponds to the extraction of 3 cores. The analysis conducted by Dynamic Shear Rheometer (DSR) requires less material and was postulated to provide us with similar data. Therefore, the aged and rejuvenated binders were characterized for their viscous properties by means of Penetration test at 25 °C, as well as by a DSR sweep with the plate-plate system, using temperatures ranging from 10 °C to 100 °C and frequencies from 0.1 rad/s to 100 rad/s (0.0159 Hz – 15.9 Hz).

Penetration was additionally estimated from the DSR results using regression equation Eq. (2) between penetration and complex modulus (G^*) [Pa] at 30 °C and 1.59 Hz developed for the standard paving grade bitumens by Nynas Oy.

$$Pen_{25^\circ C} = 260236 * G^{*-0.639} \quad (2)$$

Comparison between the measured and calculated Pen values is provided in Table 1 and 5. It was confirmed that Eq. (2) is suitable at least for straight run and aged samples. For the used blending recipe, G^* values were translated into the Pen with the help of Eq. (2), then typical blending equation Eq. (1) was applied. Such computed fractions are provided in Table 2a. Due to the communication error between laboratory staff, a target Pen was changed for second rejuvenation cycle. R1, R3 and R4 aimed at the measured Pen of B80, while R2 at the Pen calculated from the G^* .

Table 2. (a) Rejuvenation recipes calculated with the help of Eq. (1) and (2) (values rounded to the closest 0.5%) targeting Penetration values provided in Table 3. (b) The recipes for simulating the targeted binder (B80) stiffness at three performance temperatures were obtained with the help of Eq. (3).

		R1	R2	R3	R4
B800 addition (executed)					
Recipe used based on Pen 25 °C	%	33	28,5	23	21
B800 addition (simulated)					
Recipe based on G^* at 15 °C	%	27.1	17.5	9.7	6.7
Recipe based on G^* at 30 °C	%	34.4	27.6	22.7	22.5
Recipe based on G^* at 60 °C	%	45.7	40.6	37.5	<u>39.2</u>

Table 3. Target and measured Penetration values for blends.

		R1	R2	R3	R4
Penetration:					
Target	0.1 mm	86	91	86	86
Measured after blending	0.1 mm	74	79	74	72
Difference	0.1 mm	11	12	12	14

The simulated recipes in Table 2b were based on the complex modulus (G^*) at various temperatures as follows:

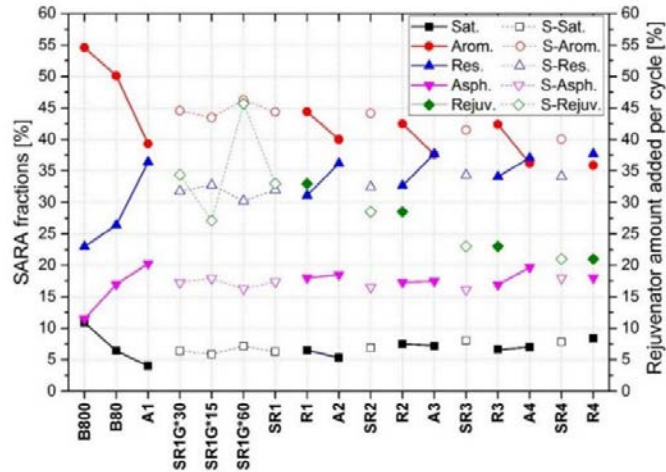


Fig. 1. SARA fractions. Measured results (B800, B80, A1-4, R1-4) along the rejuvenator content used during blending (Rejuv.) presented as filled points and straight lines. Simulated (S-) fractional composition on the basis of the rejuvenator content (S-Rejuv.) calculated from Eq. (2) (SR1-4) and based on Eq. (3) at different temperatures (SR1G*15, SR1G*30, SR1G*60), presented as empty points and dashed lines.

$$\log G_{blend}^* = a_1 * \log G_{aged}^* + b_1 * \log G_{rejuv}^* \tag{3}$$

where G_{blend}^* = Complex modulus of the blend
 G_{aged}^* = Complex modulus of aged binder
 G_{rejuv}^* = Complex modulus of rejuvenator
 a_1 and b_1 = mass fractions of aged binder and rejuvenator.

Due to the temperature- $\log G^*$ relationships for A1 and B80 not being parallel lines (further explained in section 3.3), we computed the rejuvenator mass fractions on the basis of G^* at three different temperatures as well. This allowed us to compare outputs of Pen based blending chart equation Eq. (1) with outputs of Eq. (3).

Additionally, samples were analyzed with Iatroscan MK-6 using methodology described in Simonen et al. (2013) to provide the chromatographic analysis of bitumen fractions (SARA); as well as by Gel Permeation Chromatography (GPC). For the GPC analysis a Waters 515 HPLC system, accompanied by 717 plus Autosampler, with a refractive index (RI 2414) detector, was used to measure the molecular weight (MW) distribution in samples dissolved in tetrahydrofuran injected onto the GPC columns (PL Gel 5 μ MIXED-D, 500, 100, 50 Å). Polystyrene standard was used for the calibration.

Simulated blends' characteristics (SARA, GPC and G^*) were calculated on the basis of rejuvenator to bitumen ratios provided in Table 2, in order to demonstrate the applicability of the methods in quality control. The name of the simulated results using executed percentages (Table 2a) typically starts with "S" and a corresponding sample name e.g. R1, giving "SR1" as the name of the sample. If a different mass percent of the rejuvenator was used for

computations, it is indicated in the name, e.g. “SR1G*15” means “calculated R1 on the basis of simulated rejuvenator ratio determined from G^* at 15 °C”.

3. Results and discussion

3.1. SARA-fractions

Figure 1 shows the numeric change of SARA fractions in aged and rejuvenated bitumens. Saturates are the most inert fraction which decreases slightly in aging, but the soft bitumen restores this decrease back to the original or even to a slightly higher level. Aromatics decrease in aging and the soft binder addition increases aromatics, however, the overall trend is a decrease with increasing recycling cycles. In resins, the trend is opposite in aging, the resin content increases and the soft rejuvenating binder decreases the resin content, but the overall trend is an increase. This follows the transformation observed previously in the work of Isacsson and Zeng (1997). Asphaltenes remain more or less on the same level throughout the cycles.

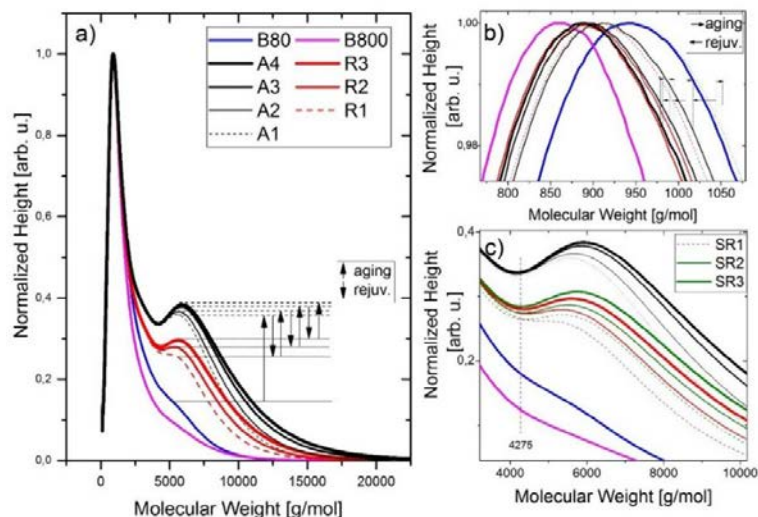


Fig. 2. Gel Permeation chromatographs after normalization - base bitumens B80 and B800, along the aged (A1-4) and rejuvenated (R1-3) samples, as compared to the calculated chromatographs based on the rejuvenator content determined from Eq. (2) (SR1-3): a) whole molecular weight range, b) maximum peak range close up, c) high molecular weight range close up.

We tried to evaluate if the determination of SARA fractions would be a good quality control method to follow rejuvenation. We have simulated (Sim) the fractional composition, assuming that fraction content is similar to the concentration of a component within bitumen as demonstrated by Simonen, et al., (2013). We used characteristics of the rejuvenator and the aged sample, along with rejuvenator’s content (Table 2), to predict the fractional composition (S-entries in Figure 1). The agreement between Sim and laboratory prepared samples was within the repeatability limits reported by Lehto (1988). It became apparent that the differences in SARA analysis between rejuvenator and base binder are very slim; thus, the numerical result of the method will not be sensitive enough to distinguish beyond doubt between quite substantial amounts of rejuvenator. For example, the predicted SARA for 27.1% and 33% rejuvenator is changing by less than the repeatability limit. The maximum recommended amount of the rejuvenator in HIPR is 3.4%, based on research by Makowska and Pellinen, (2015), and it is assumed that its’ contribution to SARA-fractions results will be minuscule.

However, it became apparent that when the rejuvenation is primarily a physical process, the fractional distribution is predictable. Looking at the results from the 4th rejuvenation cycle and comparing it with Sim results, we can

conclude that perhaps a form of chemical aging occurred during mixing. The aromatics and resin fractions are differ significantly from the simulation. In the last cycle, for example, the amount of R4 bitumen was notably less than during the preparation of R1, thus the energy to mass ratio in the process was not equal between the cycles.

3.2. Gel Permeation Chromatography (GPC)

As expected molecular weights increase in aging, and a large molecular weight shoulder is formed in the first aging step, as observed previously by Isacson and Zheng (1997) and Le Guern et al. (2010). This shoulder is between the molecular weights of 4 000 and 10 000 Da. In more recent explorations of the chemical composition of bitumen McKenna et al. (2013) have proposed that the actual molecular weight of bitumen molecules is below 2000 Da, whereas Le Guern et al. (2010) have suggested that signals which are typically assigned to a much higher molecular weights may be due to the agglomeration of asphaltenes. While the literature review does not confirm beyond the reasonable doubt whether the observed signal is true molecules or agglomerates, analysis of our data provides an additional input into the discussion.

To simulate a potential chromatograph of the rejuvenated sample, simple curve mathematics (normalization and weighted average) were applied on initially normalized collected (Col) chromatographs after Strate (1978) and Segal (1968). Thus in Figure 2a, the changes can be clearly seen in the ratio of the high molecular weight (HMW) components to the low molecular weight (LMW) components. In the first aging stage, the increase in HMW is the most substantial and rejuvenation decreases the HMW/LMW ratio. The actual ratio, as witnessed by smaller (HMW) peak's maximum, is lower than predicted (Figure 2c), which may be indicative of an increased dispersive forces inflicted by the rejuvenator, thus providing proof for the agglomeration during aging. We assumed that the Col curves would be above corresponding Sim curves, due to the aging during mixing. The Sim and Col curves for the rejuvenated samples differed significantly only above 4275 Da, and below this cut off a rather good fit was achieved.

Simulation aside, aging in the consecutive cycles does not seem to have such a great effect on the HMW/LMW ratio as in the first cycle, while rejuvenation seems to be on a relatively comparative level in each cycle. The position of the maximum of the main peak (MP) is affected only slightly during aging, and in each consecutive cycle the effect is lower (Table 4). The position of the MP could be very accurately predicted for rejuvenated samples by calculations based on the rejuvenator content (Figure 2b, Table 2). Additionally, for the SR1G*15 and SR1G*60 the position of the MP would be 919 and 896, respectively (compare with Table 4). Sim for 3% addition of B800 to A1, similar to the levels in HIPR, results in the shift of MP from 950 to 937. The difference between 1 and 3% was not observable by means of MP. However, the shape of the shoulder above 3300 Da (HMW) is changing significantly for a rejuvenation to be observable even at 1 to 3% rejuvenator addition. It is therefore sustained that GPC is the most promising quality control tool of the rejuvenation process. Further efforts should demonstrate the applicability of this method.

Table 4. Molecular weights of the aged and rejuvenated binders. Values in parentheses are collected from the simulated spectra (ratio from Eq. (1)), which is partially presented in Figure 2 c. The abbreviations used denote: number average molecular weight (M_n); weight average molecular weight (M_w); molecular weight of the main peak's maximum (MP) and width of the molecular weight distribution (Polydispersity = M_w/M_n).

	B80	A1	R1	A2	R2	A3	R3	A4	B800
M_n	683	737	693	715	697	728	701	739	649
M_w	1175	1519	1340	1539	1390	1606	1446	1649	1071
MP	941	950	905	910	895	896	885	887	862
MP calculated			(905)		(892)		(883)		
Polydispersity	1.7	2.1	1.9	2.2	2.0	2.2	2.1	2.2	1.6

As is presented for example in the work of Zaumanis et al. (2014), in the typical Reclaimed Asphalt Pavement reuse, oil type rejuvenators are primarily chosen. It is conceivable that the GPC technique could be a potential quality control (QC) tool for blends with such products, as they are characterized by a vastly different molecular weight distribution. However, as can be observed in the data presented here, even with the rejuvenator of a molecular weight distribution curve extremely similar to the base bitumen, GPC is a promising QC technique. The amount of rejuvenator

added can be established on the basis of the shape analysis of the chromatograph, especially in the LMW region. The additional analysis of the change in the HMW's peak area (3200+ Da) during the rejuvenation stage was conducted. The choice of this cut off was based on the visual evaluation of the point where chromatographs start to differ. The results were 31.9 %, 28.7% and 26.1%, for 1st, 2nd and 3rd cycle of rejuvenation, respectively. This, at least in the first two cycles correlates well with the actual amount of rejuvenator used. The cumulative content of the rejuvenator in each sample is supposedly 33%, 52% and 63%, for the 1st, 2nd and 3rd cycle of rejuvenation respectively. As suggested earlier, the HMW peak most likely originates from the formation of nanoaggregates. If those were truly large molecules, the physical process such as rejuvenation would not lead to a decrease in their relative content within a material. It is more likely that the substantially large amount of the rejuvenator leads to different dispersion characteristics within rejuvenated materials, dispersing some nanoaggregates, and that the effect is relatively larger with high rejuvenator content. However, this particular rejuvenator does not allow for complete re-dispersion of those clusters, moreover, in every consecutive cycle, the relative amount of the assumed nanoaggregates is higher. Since the viscosity was controlled for during blending, this will most likely lead to the increase in elasticity. It is possible that for low amount of rejuvenator (as in HIPR) this dispersive effect diminishes and increase in elasticity is larger.

Nevertheless, it is envisioned that for rejuvenators with molecular weight distribution utterly differing from the base bitumen, it will be much easier to point out the presence and amount of rejuvenator added. It is also plausible that a complete re-dispersion is achievable with a different rejuvenator. Caution is advised, that in order to apply GPC in QC, one needs to optimize for their own materials and typical amounts of rejuvenator used.

3.3. Rheology

First of all, the difference in target penetration and measured penetration is due to hardening during mixing, which took place at 145 °C lasting 30 minutes, and it was partially confirmed by conducting a blank mixing test on B80. Additionally, all of the applied methods of characterization imply that the most aging took place during the first aging step. The simplest way to demonstrate the difference is to look at the Penetration values. The aged binder increased from 30 pen in the first step to 44 pen in the fourth step, even though the target and measured values for each rejuvenation stage were similar (Table 5). Although the penetrations of the rejuvenated binders are similar, the calculated softening points (temperature where $G^* = 150$ Pa at 0.0159Hz) are increasing with the recycling steps, indicating possible reheating problems in consecutive cycles. The resistance to permanent deformation is higher for rejuvenated samples in comparison with B80, but the number of rejuvenation cycles seems not to affect significantly.

Table 5. Properties of the aged and rejuvenated binders. The underlined values denote change in observed pattern of softening with consecutive stages of aging and rejuvenation. The values used for PG-grading are provided in bold. The values in parentheses were calculated for the samples and presented as a comparison to the original binder, but are not considered for PG-grading.

		A1	R1	A2	R2	A3	R3	A4	R4
DSR, G^* at 15 °C, 1.59 Hz	[Pa]	$1.45 \cdot 10^7$	$3.94 \cdot 10^6$	$8.36 \cdot 10^6$	$2.86 \cdot 10^6$	$5.83 \cdot 10^6$	$2.78 \cdot 10^6$	$5.17 \cdot 10^6$	$2.85 \cdot 10^6$
DSR, G^* at 30 °C, 1.59 Hz	[Pa]	$1.71 \cdot 10^6$	$3.19 \cdot 10^5$	$1.03 \cdot 10^6$	$2.54 \cdot 10^5$	$7.53 \cdot 10^5$	$2.74 \cdot 10^5$	$7.43 \cdot 10^5$	$3.09 \cdot 10^5$
DSR, G^* at 60 °C, 1.59 Hz	[Pa]	$1.96 \cdot 10^4$	$2.30 \cdot 10^3$	$1.21 \cdot 10^4$	$1.91 \cdot 10^3$	$9.30 \cdot 10^3$	$2.35 \cdot 10^3$	<u>$1.07 \cdot 10^4$</u>	<u>$3.04 \cdot 10^3$</u>
δ at 30 °C, 1.59 Hz	[°]	48	63	50	62	50	59	48	56
Measured Pen	[0,1 mm]	30	74	39	79	43	74	44	72
Pen Calc. from Eq. (2)	[0,1 mm]	27	77	37	92	46	87	46	81
Calculated S.P. ²⁾	[°C]	66.4	50.0	62.7	49.7	60.5	51.6	62.9	54.4
$G^*/\sin\delta = 1$ kPa	[°C]	(82)	68	(79)	67	(78)	68	(79)	69
$G^*\sin\delta = 5000$ kPa	[°C]	20	(14)	16	(12)	14	(11)	13	(11)

The Black curves (Figure 3) of both the aged and rejuvenated binders show that the binders become more elastic with each step. After each recycling step, the phase angle becomes slightly smaller at a certain complex modulus (G^*) level, and rejuvenation is not able to restore the viscous properties. This is very clearly seen in Figure 4a where the phase angle decreases from cycle to cycle, although the penetration level of the rejuvenated binder is the same.

When rejuvenated, the blend with the aged binder reaches the $G^*(30\text{ }^\circ\text{C})$ level of the fresh binder and the rejuvenation seems to restore some of the original physical properties (Table 5, Figure 3 and 4).

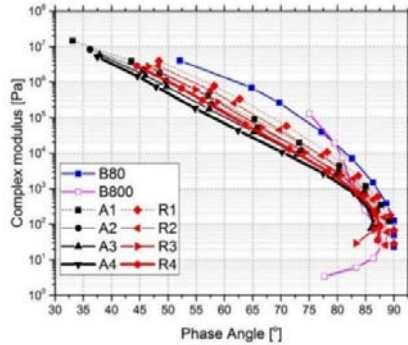


Fig. 3. Black curves for aged and rejuvenated binders.

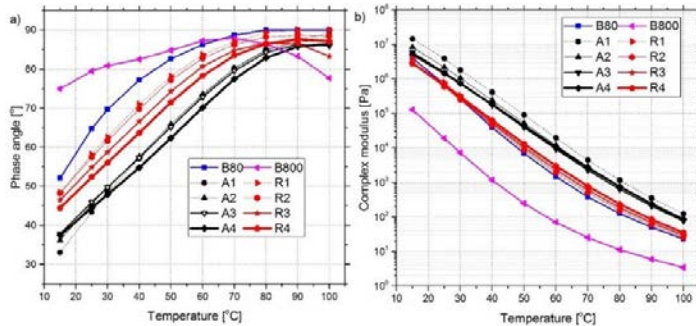


Fig. 4 a) Phase angle (1.59 Hz) development in increasing rejuvenation (thickening red lines) and aging (thickening black lines) steps; b) Complex modulus at frequency of 1.59 Hz as a function of temperature for all tested samples in comparison with the original binder and rejuvenator.

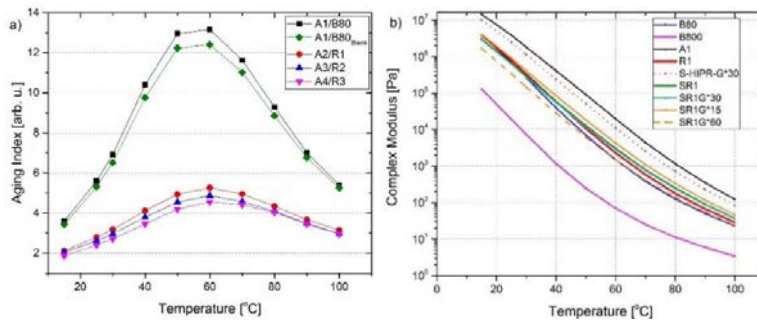


Fig. 5 a) Aging index in different recycling cycles at the frequency of 1.59 Hz.

Aging index = $G^*_{aged}/G^*_{rejuvenated}$. b) Demonstration of the effect of the choice of optimization temperature on the complex modulus of blends. Simulations conducted on the basis of Eq. (3)

Rejuvenator mass percentages are calculated based on Pen25 °C, at that temperature, the complex modulus values seem to be close to those of B80 (Figure 4 b). At high temperatures, the rejuvenated binders have a higher G^* , but at a lower temperature, the rejuvenated binders have a lower G^* than the fresh reference binder. The SHRP critical temperature decreases in the first 2 rejuvenation and aging cycles, but it increases in the last two. However, the low

temperature susceptibility of the binder steadily decreases with increasing recycling cycles, leading to the overall improvement of the temperature susceptibility of G^* .

It is assumed that during aging more oxidation, agglomeration and cyclization is occurring, and those chemical changes are irreversible by a physical process such as rejuvenation with the soft binder. This is similarly visible in GPC as when the penetration of the rejuvenated bitumens is equal, their molecular weight distributions are significantly different, meaning that two materials being rheologically similar at given temperature, may have a different chemical composition and behavior at temperatures other than the one compared. This has been repetitively demonstrated by e.g. Baginska and Gawel (2004) and Karlsson and Isacson (2002) for different crude oil sources. We hereby have demonstrated that with a different history of aging and rejuvenation of the sample, the same holds true.

It is interesting to note that the aging measured with the complex modulus based aging index (Figure 5a) decreases with the increasing recycling cycles. The difference is partially explained by the binder hardening during the blending stage. The same mixing hardening is not included in the first, fresh binder aging index. However, in a blind reference test where fresh B80 was mixed alone for 30 minutes at 145 °C, the penetration decreased from 86 to 81 and the calculated aging indexes decreased only a little. Regardless, the aging seems to be relatively lower when the recycling cycles increase and the first aging cycle seems to be the most severe. Similar is also observed from the retained penetrations as well as SARA fractions and GPC results (Figure 1 and 2, Table 5). This artifact is most likely due to the fact that the amount of rejuvenator used was on such extremely high level. After 3rd rejuvenation cycle, the concentration of original B80 should be on the level of 36.9% and that means that the aging characteristics of the rejuvenator (see Table 1) are dominant and perhaps drastically different than those of a base bitumen.

As presented in Figure 5b and Table 2, if a value of complex modulus is used for the purpose of the optimization, the temperature at which complex modulus is selected plays an important role. We demonstrate how the calculations according to Eq. (3) would lead to a different suggested rejuvenator content if 3 different temperatures, namely 15, 30 and 60 °C (Table 2), were used. Afterwards, using the same equation and obtained rejuvenator fractions, we calculated complex modulus at different temperatures ($G^*(T)$) of the fictitious blends, later denoted as simulated (Sim). The results of those calculations are visualized in Figure 5b as well. It became apparent that the aged and fresh straight run bitumens $\log G^*(T)$ characteristics are not parallel lines: they have different temperature susceptibility, therefore, caution is advised. Interestingly, according to simulations if the high temperature G^* is used for the optimization, we should obtain blends softer at low temperatures while retaining the high temperature characteristics. Conversely, optimizing for the G^* at very low temperature would lead to increased stiffness at high temperatures in the obtained blends. $G^*(30)$ plot was very close to that obtained for G^* calculated from Penetration ratios, and as such we suggest that they are approximately exchangeable. $G^*(30)$ can be used in the absence of Penetration values. Additionally, when one compares SR1 characteristics with R1 blend, the G^* characteristics are lower at high temperatures and higher at low temperatures. This would indicate that using high temperature G^* , like $G^*(60)$, could result in a product softer at high temperatures than desired.

To sum up, the rejuvenation of aged bitumens, executed according to the ratios determined from intermediate rheological characteristics, allows for the recovery and even apparently improvement (Figure 4b, Table 5) of low temperature properties, while enhancing resistance to deformation, as also demonstrated in the studies reported on the first recycle stage by Kennedy et al. (1998) and Romera et al. (2006). This is typically desired in the cold climate, as well as for heavy traffic. However, caution is advised as the study presented here chose the rheological characteristics of straight run B80 as the target. Using this binder grade as the target may inflict susceptibility to rutting in Finnish climate. The amounts of rejuvenator typically used on the road as discussed by Makowska and Pellinen (2015), especially in HIPR are much smaller than those used in this laboratory study, and yet roads exhibit rather good performance in service. We have also calculated the $G^*(T)$ characteristics for HIPR process (i.e. maximum rejuvenator and admixture amount used in Finland), using the straight run values for B80 and B800, Figure 5b. McDaniel et al. (2002) suggest aiming in optimization at the properties of the short-term aged bitumen (e.g. only RTFO treated) for which unfortunately the DSR analysis was not conducted in this study.

The low temperature properties should be better for the rejuvenated binders compared with B80 because of the lower complex modulus at low temperatures. However, as the elasticity of bitumen increases, the stress relaxation capacity decreases which may counteract the improvement. The complex modulus of the rejuvenated binders at 15°C is decreasing in each recycling cycle step i.e., bitumen becomes softer and the same takes place for the consecutively aged blends.

4. Conclusions

Fresh bitumen changes the most in the first aging step with considerably less aging occurring in the following aging steps. In aging, a signal consistent with the formation of large molecules is witnessed by GPC. Although SARA-fraction analysis indicates that aromatics change to resins, as in typical aging, the soft rejuvenator balances the fractional composition to some degree (restoration of asphaltene and saturate content).

In practice, the physical properties can be restored close to the original state or, in some respects, the rejuvenator can improve the properties of the binder, such as the temperature susceptibility of the complex modulus. The changes cannot be chemically reversed, because oxidation of bitumen (chemical reaction) cannot be reversed by mixing aged product with a non-reactive rejuvenator (physical process), such as soft bitumen.

The analytical technique of GPC was demonstrated as a good candidate for the quality control of the rejuvenation process. Complex modulus is recommended to be used in blending calculations and it provides reasonably accurate results. Therefore the equation (3) is suggested for use. The choice of the optimization temperature is still debatable leading us to suggest that considerations be made for specific climate and traffic characteristics.

The properties of the aged binder are still very close to the properties of the fresh binder after four recycling cycles, suggesting the viability of multiple asphalt recycling. The most important in rejuvenation is to set a target property and optimize the blend towards it, ensuring that the other important properties are not compromised. In this study, a soft binder B800 is used for rejuvenation and the amounts needed were between 21 - 33% of the aged binder. The future research should focus on the evaluation of the effect of softer bitumens, such as V1500, or oil based rejuvenators to mitigate the overfilling of voids and bleeding; investigate if the observed changes agree for other binders of different crude oil origin and for polymer modified bitumens. In addition, because of different raw materials and performance histories, there is also a need to consider the most appropriate rejuvenators according to the life-cycle of the bitumen at hand in a case-by-case basis.

References

- (PANK), F. P. (2000). *Finnish Asphalt Specifications 2000*. Helsinki: Edita Ltd.
- Baginska, K., & Gawel, I. (2004). Effect of origin and technology on the chemical composition and colloidal stability of bitumens. *Fuel Processing Technology*, 85, 1453-1462.
- Isacsson U., Zzeng H. (1997). "Relationships between bitumen chemistry and low temperature behaviour of asphalt." *Construction and Building Materials*, vol. 11, no. 2, 83-91.
- Issariyakul, T., & Dalai, A. (2014). Biodiesel from vegetable oils. *Renewable and sustainable Energy Reviews*, 31, 446-471.
- Karlsson, R., & Isacsson, U. (2002). Bitumen Rejuvenator diffusion as influenced by ageing. *Road Materials and Pavement Design*, 3:2, 167-182. doi:10.1080/14680629.2002.9689920
- Kennedy, T.W., Tam, W.O. & Solaimanian, M. (September 1998). *Effect of Reclaimed Asphalt Pavement on Binder Properties Using the Superpave System*, Research Report FHWA/TX-98/1250-1, South Central Superpave Center, Austin: The University of Texas
- Le Guern, M., Chailleux, E., Farcas, F., Dreessen, S., & Mabilie, I. (2010). Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging. *Fuel*, 89, 3330-3339.
- Lehto, E. (1988). *Bitumin fraktiointi TLC/FID-menetelmällä [Bitumen fractionation by TLC-FID method]*. Kemian laitos [Chemistry department]. Oulu: University of Oulu.
- Makowska, M., & Pellinen, T. (2015). Development of specifications and guidelines for hot in-place recycling in Finland – Outline and framework. *8th International RILEM Conference*. Ancona, Italy.
- McDaniel, R., Soleymani, H., & Shah, A. (May 2002). *Use of Reclaimed Asphalt Pavement (RAP) Under Superpave Specifications: A Regional Pooled Fund Study*. North Central Superpave Center. West Lafayette: Purdue University.
- McKenna, A. M., Marshall, A. G., & Rodgers, R. P. (2013). Heavy Petroleum Composition. 4. Asphaltene Compositional Space. *Energy Fuels* vol. 27, 1257-1267.
- Romera, R., Santamaria, A., Pena, J.J., Munoz, M.E., Barral, M., Garcia, E. & Janez, V. (2006) Rheological aspects of the rejuvenation of aged bitumen. *Rheol Acta*, Vol. 45, pp. 474-478
- Segal, L. (1968). Characterization of Celluloses by Gel Permeation Chromatography. *Journal of Polymer Science: Part C*, 21, 267-282.
- Simonen, M., Blomberg, T., Pellinen, T., Makowska, M., & Valtonen, J. (2013). Curing and aging of biofluxed bitumen: A physicochemical approach. *Road Materials and Pavement Design*, Vol. 14, No. 1, 159-177.
- Strate, G. V. (1978). Structure Characterization in the Science and Technology of Elastomers. In F. R. Eirich, & B. E. James E. Mark (Ed.), *Science and Technology of Rubber* (pp. 75-155). New York: Academic Press Inc.
- Zaumanis, M., Mallick, R., Poulidakos, L., & Frank, R. (2014). Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures. *Construction and Building Materials*, 71, 538-550