Sustainability & Environment

Binder and mix aging with Polymer modified Bitumen – a laboratory evaluation

Porot Laurent, Jellema Erica, Kluttz Robert
Kraton Polymers

Abstract

Polymer modified Bitumen (PmB) has been commonly used for more than 40 years in the paving industry. It brings multiple benefits to the road with high performance in the materials, especially with higher rutting resistance, high cracking performance and overall better durability and reliability in the road. At the same time, the reuse of old asphalt pavement into new asphalt materials is becoming common practice. On a long-term perspective the benefits of having PmB in pavement and to be further reused at the end of the life is not widely considered. Most often Reclaimed Asphalt (RA) is reused in the same way whether it contains polymer or not. There are already some testing protocols used to characterise the aging of the binder and they are part of current material specifications. However, more research efforts are made to consider, not only aging on binder alone, but in the complex materials of asphalt mix. This paper presents some comparative results on both binder and asphalt mix with laboratory aging protocols. It was conducted on two different PmB, one having a 3.5 % moderate level of SBS polymer and one having a high level of modification. These PmBs were compared with a standard paving unmodified binder. The binders themselves were subject to short-term aging with RTFOT and further long-term aging with Pressure Aging vessel (PAV). The asphalt mixes were subject to short-term and long-term aging in oven. From the mixes, the binder was extracted and recovered at different periods of time for further characterisation. In addition to physical properties, the chemical changes were tracked using FTIR. The outcomes demonstrate the long-term benefit and potential recyclability of SBS modification at both binder and asphalt level.

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1 INTRODUCTION

Polymer modified Bitumen (PmB) has been developed and fully implemented since the 80's. For paving application, the majority of modification is with Styrene-Butadiene-Styrene block copolymer. It is now standard practice to use PmB, bringing superior characteristics for asphalt pavement with higher rutting resistance and cracking performance [1]. Specifications, either in Europe with the EN 14023 or in US with Performance Grade, define the essential characteristics of the binders at original stage and over-short and long-term aging.

Over the last decades, asphalt recycling and reuse of Reclaimed Asphalt (RA), have become also standard practice, bringing economic and environmental benefits [2]. For base layer, using conventional paving grade bitumen, recycling is well-defined and go up to 50 % or above. For mature road networks, there is a coming need for reusing surface layer into surface layer, taking advantage of high quality aggregates and PmB, when used up front. Today, the current practice is conservative, limiting the reuse of RA around 20 % for surface layer. One limiting factor is the RA mineral parts, with both quality and grading. The other limiting factor is the RA binder. For the reuse of RA not containing polymer, making polymer-modified asphalt mix will lead to an insufficient polymer content with standard PmB. Special PmB will be required, having higher polymer content to compensate the eventual deficit of polymer from the RA binder and to ensure similar long-term behaviour. For RA that contains PmB, the question is, will the polymer from the binder still be present and bring the same performance level at end of the life, to be considered as PmB for the next use.

Aging of PmB has been evaluated in different researches on binder [3] [4]. Different polymers, elastomer or plastomer, have been reported behaving differently [5]. It showed that beyond the conventional properties, the rheology of the materials in various conditions is key and for aging and Infra-Red can address the chemical structure where the polymer can be tracked and the level of oxidation. Those characterisations help in defining laboratory experiment for bitumen aging.
To address aging of binder, short-term aging with Rolling Thin Film Oven Test (RTFOT) and long-term aging through Pressure Aging Vessel (PAV) are commonly used. However, PmB usually displays higher viscosity than pen grade bitumen and, during RTFOT, the binder does not always form a thin film in the bottle and thus is not always suitable for addressing real short-term aging during mixing process.
Having aging on asphalt mix itself will be closer to true aging during mixing, and more appropriate. The interaction with aggregates, mixing process and aging condition, are foreseen as complementary information to the binder aging. In recent years, lab mix aging protocols have been developed [6] and the Rilem has set up an experiment [7] used now as an agreed protocol to age loose asphalt mix, short and long-term. While the short-term aging appeared more aggressive as compared to RTFOT [8] it provides a reasonable approach when comparing different materials together.

Asphalt mix aging with PmB has been started to be studied [9] with different aging protocol. As compared to paving bitumen, aging of PmB has shown similar trend with hardening effect and somehow slight loss of ductility. On the other hand, studies comparing lab binder aging and field data [10] showed a lower degree of aging as compared to lab prediction, still a hardening effect but less than forecasted in laboratory.
Considering aging, asphalt mix, complex bitumen such as PmB, there are a multiplicity of parameters. The experiments done so far were with different types of bitumen and not always well- known polymers or polymer concentrations. Thus to really evaluate and quantify the effect and long-term contribution of SBS in binder and mix it is important to keep control of the different parameters.

This paper presents and compares results of aging on binder and asphalt mix, when considering SBS PmB. A standard paving grade bitumen was compared with two PmBs at low and high SBS content. In addition to conventional testing, the rheology of the binders were assessed over the different stages of aging, and infra-red spectrometry done to track the evolution of the chemical species.

2 EXPERIMENTAL PLAN

2.1 Materials

In this study, three different binders were considered, a reference 50/70 neat bitumen as per EN 12591, a 45/80-55 PmB with 3.5% SBS polymer as per EN14023 and a highly modified bitumen with 7.5% SBS graded as 25/55-80 as per EN14023. The standard PmB was prepared in laboratory with a soft base bitumen, 70/100 and 3.5% of Kraton D1101 SBS copolymer. The second PmB was a highly modified bitumen, HiMA, made with the reference bitumen 50/70, and 7.5% Kraton D0243 SBS copolymer. This high polymer content ensures to have a rich polymer phase in the binder, behaving more like polymer than bitumen. The polymer used was a high vinyl linear SBS polymer, with a low molecular weight, enabling keeping the viscosity of the final PmB in reasonable range for manufacturing asphalt mix. It has been developed to enhance further the rutting resistance and cracking performance for either surface layer or structural layers [11]. Table 1 displays the main properties of the three binders used in the study.

Table 1. Main properties of binders

Binder	Label	EN Grade	Formula	Penetration value at 25°C	Softening point temperature
Bitumen 50/70	50/70	50/70	50/70	58x0.1mm	48.2°C
Standard PmB	PmB	45/80-55	70/100+3.5D1101	62x0.1mm	57.8°C
HiMA PmB	HiMA	25/55-80	50/70+7.5%D0243	33x0.1mm	88.5°C

Hot mix asphalt was produced in the laboratory with the three binders. The mix was a dense asphalt mix using four different aggregate fractions. The binder content was 5% per weight of aggregates, 4.76% of total mix. For each mix, 12 kg was manufactured per batch of 3 kg, produced with the same mixing protocol at 160°C for 3 minutes. Figure 1 displays the mineral composition of each mix.

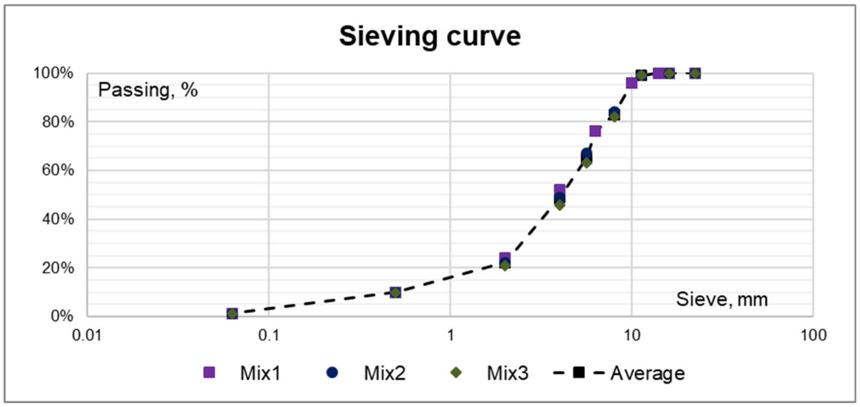

Figure 1. Asphalt mix composition

2.2 Aging protocol

The binders were aged with RTFOT, according to EN12607, and PAV, according to EN14769. They correspond respectively to short-term aging, occurring during manufacture, transport and laying, and long-term pavement aging under road conditions [12]. While it is not always recognised as exactly mimicking the real aging conditions, it provides indications on aging behaviour.

For laboratory asphalt mix aging, the Rilem protocol was used [7] consisting of

- "Short-term" aging on loose mixes in an oven at 135°C for 4 hours
- "Long-term" aging on loose mixes in oven at 85°C

Samples were collected after short-term and long-term aging at 5, 7, 9, 12 and 20 days enabling to monitor the aging over a wide range of time. Binder was extracted and recovered, using trichloroethylene, according to EN12697-3.

2.3 Bitumen evaluation

For binder evaluation, conventional characterisation was made according to EN12591 and EN14023 with penetration value at 25°C, as consistency at ambient temperature, and with softening point temperature, as consistency at high temperature. On the original binders the Fraass breaking point temperature, Brookfield viscosity and elastic recovery were also measured.

In addition, more fundamental testing was performed using Dynamic Shear Rheometer (DSR) in temperature ramp from -20°C to +90°C at 10rad/s with a 10mm plate, 2.5mm gap. This enabled to have the full rheological behaviour of the materials over a wide range of temperatures. Furthermore, Fourier Transformed Infra-Red spectroscopy (FTIR) in Attenuated Total Reflectance (ATR) mode was done on each sample.

3 RESULTS WITH BASIC PROPERTIES

3.1 Binder evaluation

The three binders were characterised according to EN14023 including the resistance to hardening. Table 2 displays the results.

Table 2. Binder basic properties

Property	Test method	Unit	Bit 50/70	PmB	HiMA
Essential requirements					
Penetration value at 25°C	EN1426	x0.1mm	58	62	33
Softening point temperature	EN1427	°C	48.2°C	57.8°C	88.5°C
Penetration Index			*-1.32*	*1.12*	*4.34*
Resistance to hardening (RTFOT)					
Change of mass	EN12607	%	0.08%	0.00%	0.12%
Retained penetration	EN1426	%	60%	76%	82%
Increase in softening point	EN1427	°C	6°C	3°C	1°C
Additional requirements					
Fraass Breaking point temperature	EN12593	°C	-13.6°C	-19.4°C	-18.5°C
Plasticity range		*°C*	*62°C*	*76°C*	*108°C*
Elastic recovery at 25°C	EN13398	%	8	87	87
Elastic recovery at 25°C after RTFOT	EN13398	%	8	75	85
Dynamic viscosity at 135°C	EN12596	$mPas^{-1}$	356	1180	3160

PmB and HiMA displayed a high softening point with still very low Fraass breaking point. This leads to a plasticity range, as the delta between both temperatures, of 76°C and 108°C respectively for the PmB and the HiMA binder, versus 62°C for the 50/70, as seen in Figure 2. Furthermore, as compared to the neat 50/70 bitumen, the PmB and the HiMA binder displayed a high elastic recovery as measured at 25°C even after RTFOT, it remained above 70% for the PmB and 80 % for the HiMA. If the SBS polymer network would have been affected by short-term aging, its ability to recover elastically would have decreased significantly.

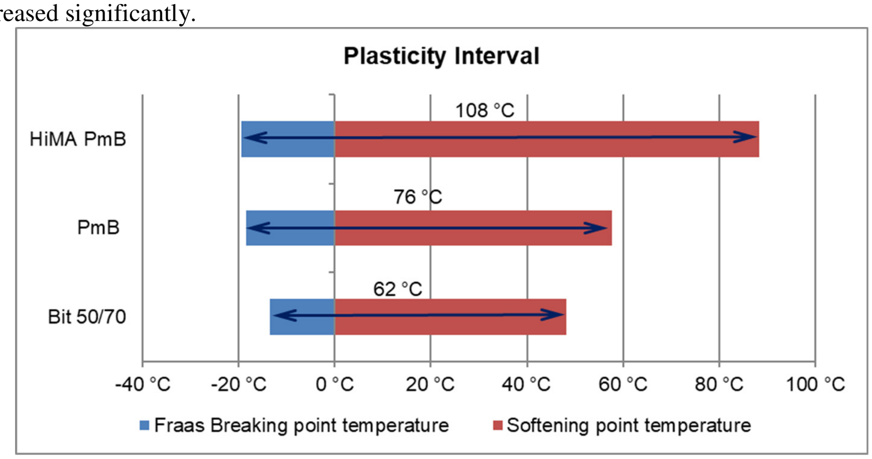

Figure 2. Plasticity interval for the three binder 50/70, PmB and HiMA

Another way to display the properties for original binder is to use the Bitumen Technical Data Chart [13] as plotted in Figure 3.

The first top part provides indication of the consistency and temperature susceptibility for the conditions of road use, with Fraass breaking point, penetration value and softening point. PmBs have a lower temperature susceptibility, less change in properties for the same temperature range. This is enhanced for the HiMA.

The bottom part is related to elevated temperature viscosity. For normal paving grade bitumen, the data results in a straight line between penetration and viscosity scales as seen for the 50/70. This was almost the case as well for the PmB; with higher softening point, it lead to higher viscosity. However, for HiMA, there was a breakdown in both lines, between the penetration and the viscosity scales, resulting in a lower viscosity than expected if it would have been a straight line. This is mostly due to the nature of the low molecular weight high vinyl polymer.

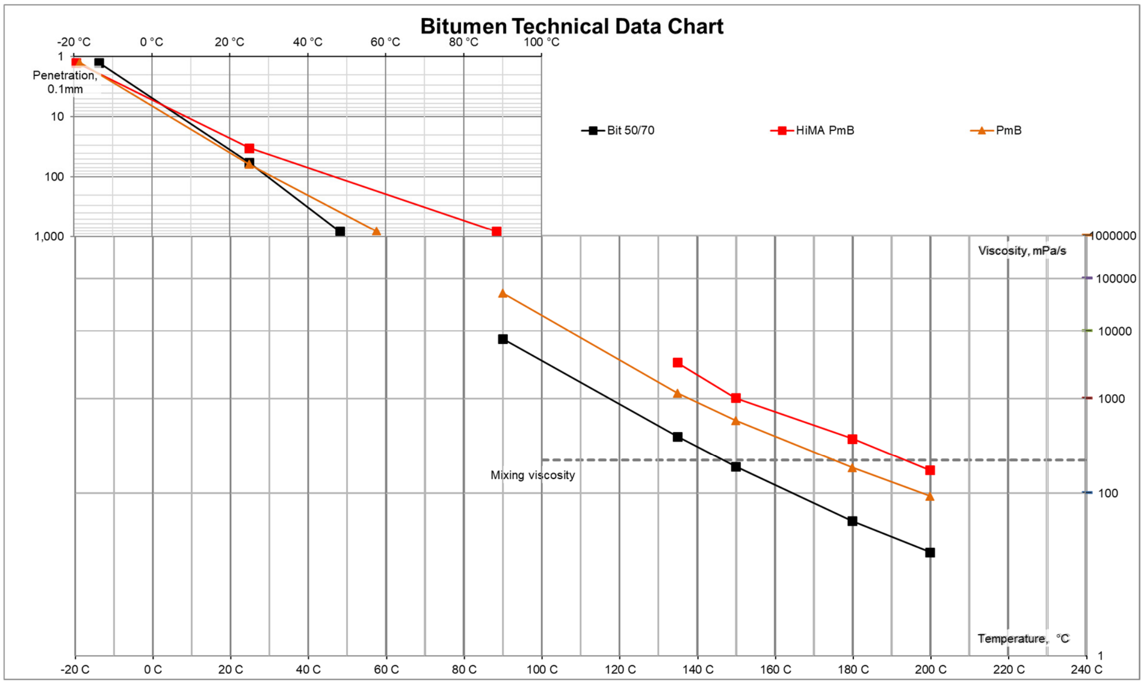

Figure 3. Bitumen Technical Data Chart for the three binders

PAV after RTFOT was also performed on the binders and the properties measured. Figure 4 displays the evolution of penetration value vs. the softening point, with, from top left to bottom right, original, RTFOT and PAV. During aging, all binders became harder but not to the same extent. The 50/70 bitumen had the greatest change and the HiMA the smallest, especially after short-term aging. This may be an artefact of the test, since the bitumen viscosity may not allow thin film formation in the bottle.

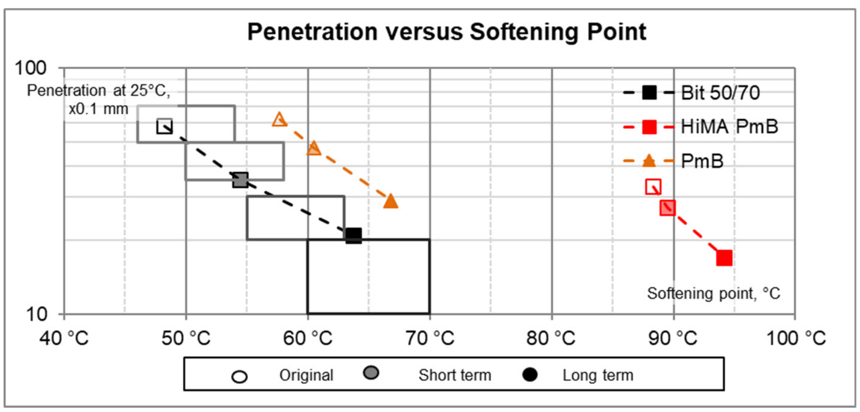

Figure 4. Change in binder properties over aging

3.2 Asphalt mix aging evaluation

During mix aging, samples were collected regularly and binders extracted recovered for further characterisation. Figure 5 displays the property change over the aging time in days, with penetration value on the left graph and softening point on the right graph. Overall, the 50/70 neat bitumen showed more change than the PmB and HiMA, especially for the short-term aging. The softening point change for HiMA was at the end of aging about 10°C while for the 50/70, which was the base bitumen used for the HiMA formulation, this was 26°C.

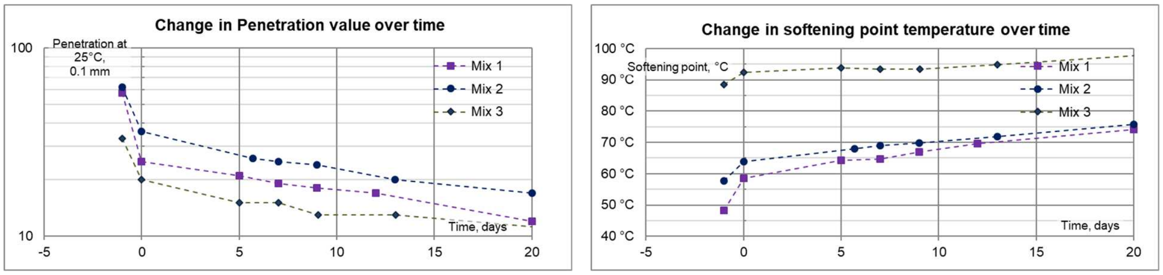

Figure 5. Binder properties after mix aging short and long-term

These values can also be compared with binder aging as in Figure 6. The dotted lines are for the mix aging and plain line for the binder aging, from left top with original and bottom right aging steps. Overall, the trend for the three binders was similar; there were no deviation between binder and mix aging lines. However, in terms of how fast the properties changed, there were some differences.

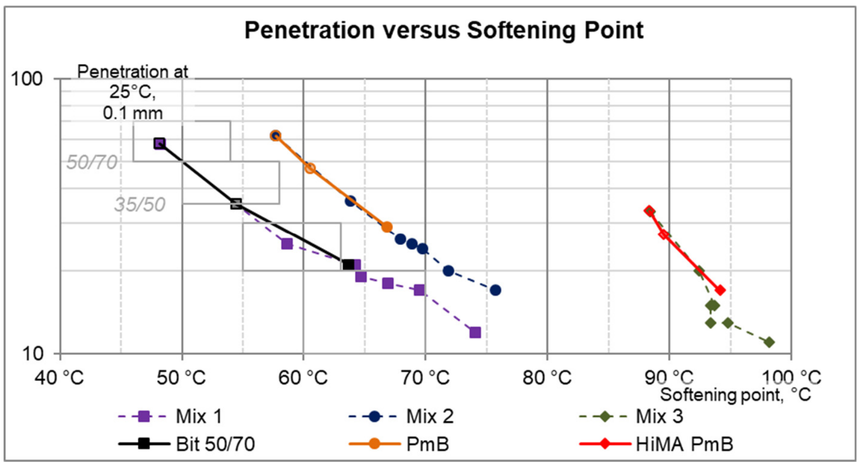

Figure 6. Change in binder properties over aging binder vs. Mix aging

The RTFOT+PAV aging status was achieved already after 5 days of mix aging. This should not be totally true as the short-term aging was more severe for the mix than for the binder, 75% lower value for penetration value and 3-4°C higher for softening point temperature, as reported in Table 3. This is something already known and reported [8] [14]. Regardless the protocol or binders, the trends between binder and mix aging are similar with the smaller property changes for HiMA, intermediate for the PmB and greatest change for the 50/70.

Table 3. Binder vs mix aging for short term aging

	50/70		PmB		HiMA	
	Pen, 0.1mm (retained, %)	Soft Pt (delta), °C	Pen, 0.1mm (retained, %)	Soft Pt (delta), °C	Pen, 0.1mm (retained, %)	Soft Pt (delta), °C
Original	58	48.2	62	57.8	33	88.5
Binder aging RTFOT	35 (60 %)	54.6 (6.4)	47 (76 %)	60.4 (2.8)	27 (82 %)	89.5 (1.0)
Mix aging 135°C, 4h	25 (43 %)	58.6 (10.4)	36 (58 %)	63.8 (6.1)	20 (61 %)	92.5 (4.0)
Mix vs. binder	71 %	4.1 °C	77 %	3.3 °C	74 %	2.8 °C

4 FUNDAMENTAL CHARACTERISATION

4.1 Dynamic Shear Rheometer measurements

Rheological behaviour of the different aged binders was further studied using DSR in temperature range of -20°C to +90°C, 10rad/s. This allows having a direct master curve without the need of shifting factor. The analysis can be made with shear modulus vs temperature, black space, or with a variety of derived parameters, such as DSR PG criteria $|G^*|/\sin\delta$, $|G^*|\sin\delta$, cross over parameters, or temperature at given $|G^*|$.

At first, the comparison of the original binders, 50/70, PmB and HiMA, is made to highlight the differences between them. Figure 7 displays the shear modulus vs. temperature for the three original binders. It provides indication on how stiff / soft is the bitumen in temperature range. From the results, it can be observed that, compared to the 50/70 bitumen, the PmB displayed lower values at low temperature, a benefit for being less brittle, and higher values at high temperature, a benefit against rutting. Overall, the variation of shear modulus with temperature is less than with the 50/70 bitumen, less temperature susceptible. In the case of the HiMA, this lower temperature susceptibility is enhanced especially for the high temperature; at intermediate and low temperature, the behaviour is similar to the 50/70 bitumen, which was used as the base bitumen.

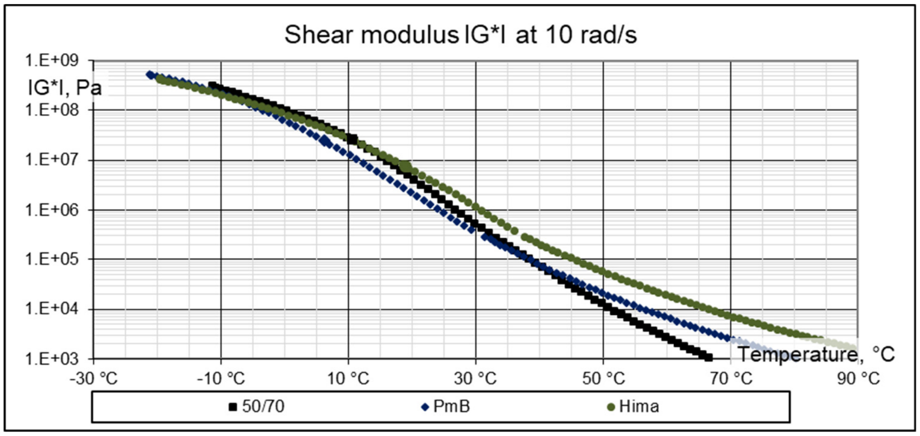

Figure 7. Shear modulus vs. temperature for original binders

On Black space, Figure 8, the phase angle, as a consequence of shear modulus, provides the rheological behaviour for elasticity, the higher the phase angle, the lower the elasticity of the material. As the graph does not have any indication of temperature, to compare like with like the data were plotted until a maximum temperature of 70 °C. With shear modulus decrease, on the left, the phase angle increases, the bitumen becomes less elastic, and therefore less able to restore deformations. This is particularly valid for the neat bitumen 50/70. With polymer modification, for low shear modulus, high temperature, the phase angle reached a plateau and the more SBS, the more elastic the bitumen remained. This is a powerful way to address SBS polymer modification.

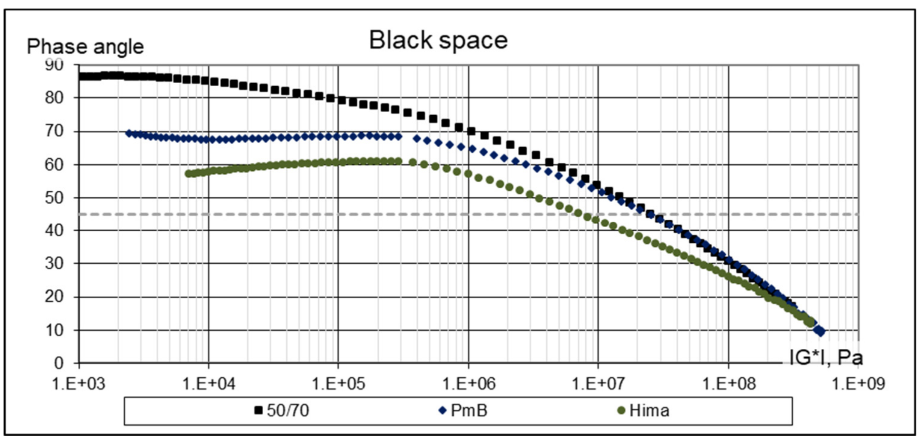

Figure 8. Black space of original binders

The effect of SBS polymer modification was tangible on both shear modulus vs. temperature and Black space but enhanced for the latter one. If the SBS is affected by aging, this will be directly visible on the Black space with loss of elasticity. To simplify the reading and prioritise the amount of data, the analysis for aging is later based on Black Space only. It is described for each binder with binder aging on the left graph and mix aging on the right graph.

Figure 9 displays the aging for the neat bitumen 50/70. With aging, the Black space curves shrank and became flatter, less concave. The shrinkage is a result of hardening; at the same temperature, the shear modulus is higher with aging. The flatness is a consequence of higher elasticity and lower temperature susceptibility. For the 50/70, the bitumen became harder and more elastic, but still the phase angle tended to reach the maximum value of 90°. Comparing the binder and mix aging, the same trend as for conventional properties was observed. The mix short term aging is more severe than the binder RTFOT aging by a factor of 4 on the shear modulus. Interestingly, for the mix, the most important change in the curvature occurred during short-term aging, the curves mostly shrank during long-term aging.

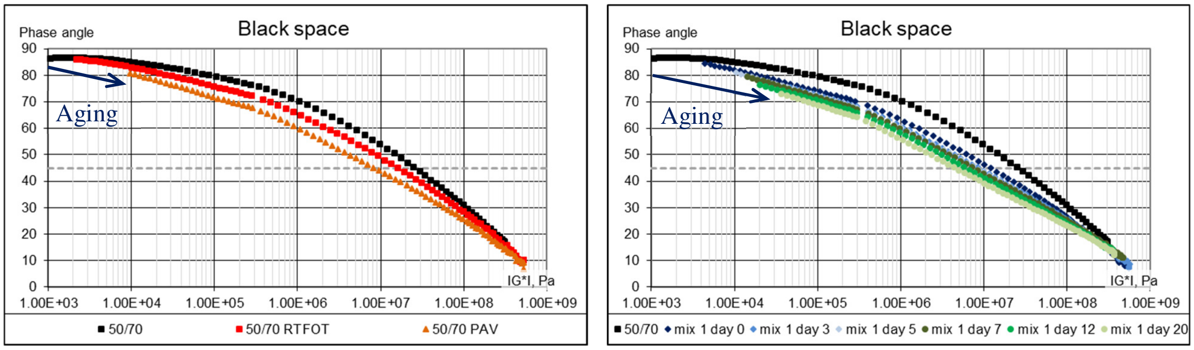

Figure 9. Black space for binder and mix aging for 50/70 bitumen

Figure 10 displays the PmB aging. The same trend as for the 50/70 bitumen was observed with shrinkage and flattening of the curves but with less amplitude. On the left part, the plateau was hardly changed and the shear modulus affected only in a factor of 2 for binder and 7 on mix aging, while for the 50/70 it was respectively 10 and 11.

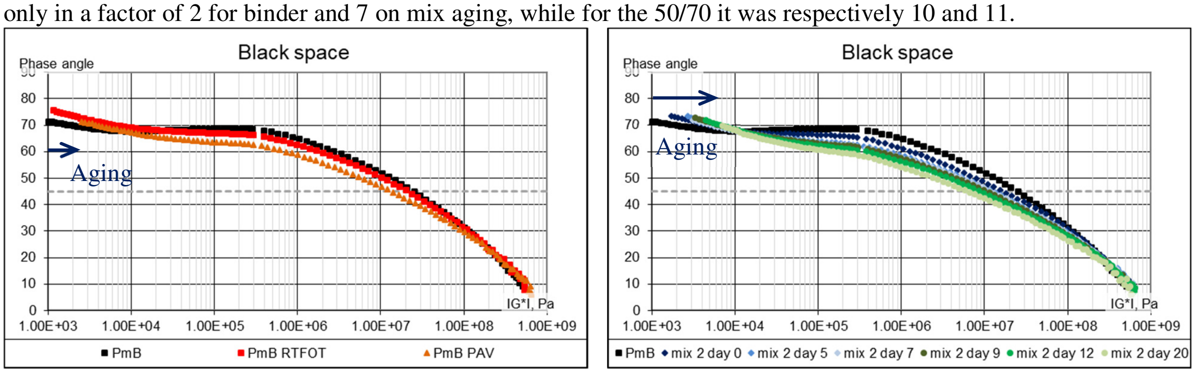

Figure 10. Black space for binder and mix aging for PmB

Figure 11 displays the aging of the HiMA binder. The results showed much lower plateau with phase angle around 60 °. Similar to the PmB, the changes were less pronounced than for the 50/70 even if it was used as the base bitumen to make the HiMA binder. Interestingly for mix aging, after the short-term aging, the curves were almost overlapping with at the end, limited effect on shear modulus and phase angle, despite the aging duration was almost double. The SBS modification effect remained recordable over aging and hardly affected.

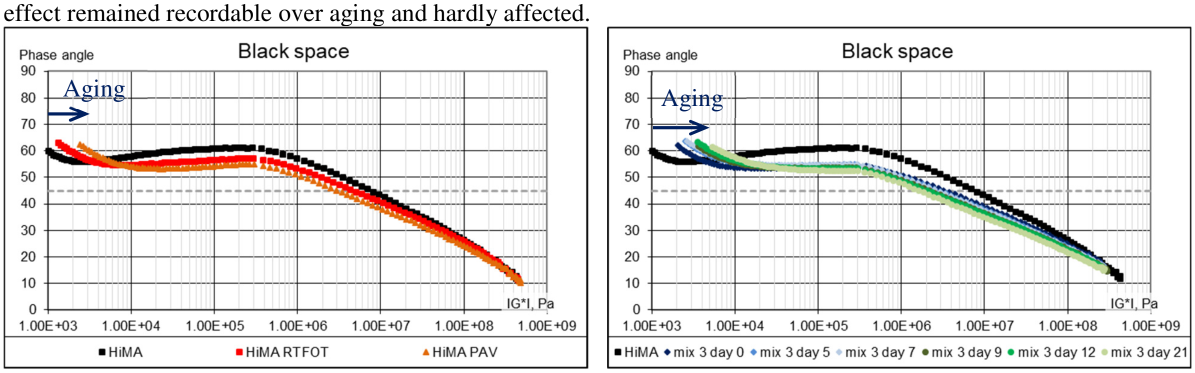

Figure 11. Black space for binder and mix aging for HiMA

4.2 Infra-Red spectroscopy

The chemical species in the bitumen were assessed via FTIR for the binders recovered from the mixes. Figure 12 shows the spectra between 2000 and 600cm^{-1} in absorbance, from top to bottom, for the 50/70 bitumen, the PmB and the HiMA binder. Comparing the PmB and HiMA with the 50/70, a peak around 970cm^{-1} can be observed, characteristic of Butadiene and did not change in intensity over aging, even after the 20days extra-aging. For the HiMA another peak is visible at 910cm^{-1}, characteristic of vinyl; and did not change during aging. The SBS polymers were still visible at the different aging stages.

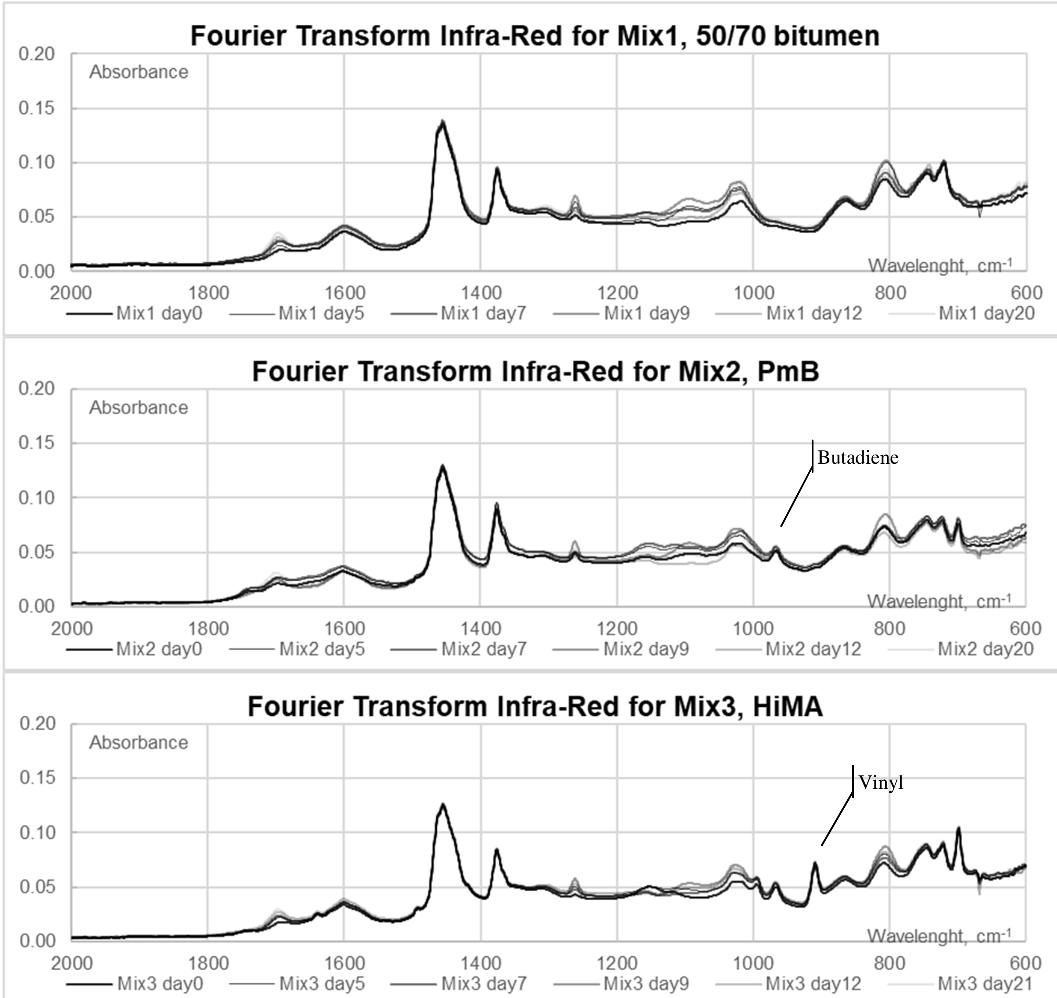

Figure 12. FTIR for mix binders, top 5070, middle PmB, bottom HiMA

For each of the binders the main changes occurred at 1700 and 1030cm^{-1} respective to carbonyl and sulfoxide groups. For comparative analysis, Carbonyl and Sulfoxide indexes were calculated as the ratio of the peak area of each group, over reference ethylene (1460cm^{-1}) and methyl (1350cm^{-1}) groups, which are not affected by aging [15]. Figure 13 shows the evolution of indexes. For all binders, the trend showed a constant increase in the carbonyl index and scattered but constant increase for the sulfoxide. This later scattering may be due to variability of the base line and boundaries of the area calculation. For the 50/70, the increase is more pronounced than for the PmB or HiMA binder even if the HiMA binder was made with the same 50/70 bitumen. It should have been expected that the base bitumen would have aged in the same way with similar increase than the neat bitumen, but the increase of sulfoxide was lower than expected.

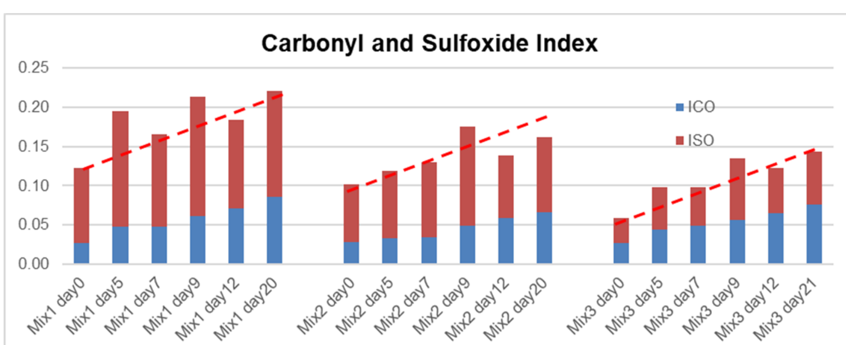

Figure 13. Carbonyl and Sulfoxide index for the three bitumen over mix aging

5 CONCLUSION

The use of PmB is well-established bringing advantages for surface layer. With the increase of interest for the reuse of RA, the question is raised how PmB will behave at end of life and can the benefits remain; can PmB mix be recyclable and how. To answer to this question, lab aging, on binder and asphalt mixes, were performed comparing neat bitumen with standard SBS PmB and highly modified bitumen.

On original properties, SBS modifications confirmed the benefits of PmB as compared to neat bitumen with high performance at high temperature against rutting, maintaining elasticity even after aging, and still good low temperature properties. With rheology, Black space can properly address SBS modification on both stiffness and elasticity where a recordable rubber plateau can be consistently observed.

Binder aging showed that, as compared to the neat bitumen 50/70, the PmB displayed smaller changes during aging and maintained the SBS benefits in terms of elastic recovery and the rubber elastic plateau. HiMA enhanced these benefits with even smaller property changes and hardly any aging effect on the Black space.
Asphalt mix aging was conducted over a period of 20 days while the normally accepted duration is only 9 days. The same trend as for binder aging was observed with smaller changes of properties over the different aging stages for the SBS modified bitumen. The key rheology features of the modified binder were maintained with recordable rubber elastic plateau, even after additional aging. If the effect of SBS polymer disappeared over aging, then the modified binder would have been behaving more like the neat bitumen, which was not the case.
The chemical structure of the binders as assessed by FTIR, did not highlight any change in the presence of SBS polymer as compared to neat bitumen over aging. The oxidation phenomenon was tracked through carbonyl and sulfoxide groups. For the three binders, there was a constant increase of the ICO and ISO; but the increase was smaller for the PmB and HiMA

In conclusion, it was observed that the SBS polymer benefits remained in the aged binders. Both binder and asphalt mix aging displayed similar trends with even smaller property changes than for standard paving grade bitumen. While neat bitumen is seen as a sustainable material that can be reused to 100 %. The same can be applied for Polymer modified Bitumen, when used on surface layer, at end of the life, the benefits are still here and confidence can be given for it to be reused with similar level of performance Later, special attention has to be made at processing at mix plant when reusing PmB RA as it may stick in mix plant drum and some aid such as rejuvenator can mitigate this drawback.

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