Evaluating the role of recycling rate and rejuvenator on the chemo-rheological properties of reclaimed polymer-modified binders

Reference:
Margaritis Alexandros, Pipintakos Georgios, Jacobs Geert, Hernando David, Bruynen Mats, Bruurs Jeroen, Van den bergh Wim.- Evaluating the role of recycling rate and rejuvenator on the chemo-rheological properties of reclaimed polymer-modified binders
Road materials and pavement design : an international journal - ISSN 1468-0629 - 22:s1(2021), p. S83-S98
Full text (Publisher's DOI): https://doi.org/10.1080/14680629.2021.1905700
To cite this reference: https://hdl.handle.net/10067/1773990151162165141

Evaluating the role of recycling rate and rejuvenator on the chemo-rheological properties of reclaimed polymer-modified binders

Alexandros Margaritis[a], Georgios Pipintakos[a], Geert Jacobs[a], David Hernando[a], Mats Bruynen[a], Jeroen Bruurs[a] & Wim Van den bergh[a]*

[a] *Faculty of Applied Engineering, EMIB research group, University of Antwerp, Antwerp, Belgium;*

*wim.vandenbergh@uantwerpen.be

Alexandros Margaritis: 0000-0003-3639-020X

Georgios Pipintakos: 0000-0002-7027-2672

Geert Jacobs: 0000-0002-8362-5609

David Hernando: 0000-0001-8284-5792

Wim Van den bergh: 0000-0002-0897-1392

Word count: 5701

Evaluating the role of recycling rate and rejuvenator on the chemo-rheological properties of reclaimed polymer-modified binders

Incorporating reclaimed asphalt (RA) is a very common practice, although its use in premium surface layer mixtures is still limited due to performance concerns. This task becomes even more challenging when combining aged polymer-modified bitumen (PMB) with virgin PMB. For this reason, the objective of this study is to evaluate, from a binder perspective, the feasibility of incorporating reclaimed polymer-modified binder (RPMB) in new surface layer mixtures. To address this challenge, blends of RPMB and virgin PMB were investigated at three replacement rates (20%, 40% and 60%) with and without a tall oil-based rejuvenator. Changes in viscoelastic behaviour were assessed through several performance indices obtained from dynamic shear rheometer testing. Moreover, physicochemical changes were tracked using infrared spectroscopy and fluorescence microscopy. The experimental investigation revealed that, due to polymer degradation of the RMPB, only the blends with 20% RMPB exhibited polymer activity. Finally, the use of the rejuvenator successfully compensated for the rheological properties of the aged RPMB and reduced the susceptibility to non-load-associated cracking but did not contribute to polymer activity restoration.

Keywords: reclaimed asphalt binder; recycling; polymer-modified binder (PMB); rejuvenator; polymer activity; rheology;

Introduction

In an era where environmental preservation becomes a necessity, the road industry has taken considerable actions towards more sustainable solutions. Asphalt recycling is a widely accepted sustainable solution, offering both economic and environmental benefits (Anthonissen et al., 2016; Aurangzeb et al., 2014). In this context, extensive research has been conducted to evaluate the performance of asphalt mixtures when incorporating high rates of reclaimed asphalt (RA), pointing out possible issues in terms of cracking performance (Zaumanis & Mallick, 2015). The main challenges when designing a mixture with RA are to restore its aged properties and to achieve the

satisfactory performance necessary for its new role in the pavement structure. Among the compensation actions typically taken are the utilisation of chemical agents such as rejuvenators and modifiers (Bajaj et al., 2020; Kodippily et al., 2017).

To date, RA has been mostly incorporated in base layers and, to a lower extent, in surface layers. Higher performance requirements for surface layer mixtures have led to a more conservative approach, although some studies have investigated the use of up to 40% in dense-graded surface mixtures (Y. Yan et al., 2017; Y. Yan et al., 2019). Still, recycling in surface layers is limited or banned by road agencies when premium mixtures, commonly produced with styrene-butadiene-styrene (SBS) polymer-modified binder (PMB), are used. That is the case of Flanders (Belgium), where their premium surface layer (stone mastic asphalt) is not allowed to be recycled into new surface layers in public works. This leads to downcycling premium RA, composed of high-quality aggregate and aged PMB, into new base layer mixtures.

A challenging task that remains is the reuse of reclaimed polymer modified binder (RPMB), as there is uncertainty in how the aged polymer participates in the new blend. An earlier study by Liu et al. showed that RPMB combined with virgin PMB exhibited some polymer-modification characteristics, but it depended on the type of RPMB and treatment (Liu et al., 2015). Given the fact that surface layer mixtures commonly use styrene-butadiene-styrene (SBS) triblock copolymer as a modifier (Yildirim, 2007), a detailed exploration for the potential reuse of this type of RPMB is still missing.

The use of rejuvenators attempts to restore the deterioration of bitumen due to ageing (Jacobs et al., 2021). What is still missing is a clear understanding of its interaction with PMB and in particular their effect on SBS degradation. The level of polymer activity and the effectiveness of the rejuvenating agent can be investigated by

assessing various rheological parameters. For example, complex modulus and phase angle master curves can reflect the temperature susceptibility of the material, especially for complex binders like PMB (Airey, 2003). Other parameters, like high-temperature true grade or parameters based on the multiple stress creep-recovery (MSCR) test, can give an indication on rutting resistance (D'Angelo et al., 2007; Domingos & Faxina, 2016). Furthermore, it has been suggested that the cracking performance of rejuvenated recycled blends can be evaluated using the Glover-Rowe (G-R) parameter (Garcia Cucalon et al., 2019; G. M. Rowe & Sharrock, 2016). Moreover, the crossover frequency (ω_c), which is the point where the viscous and elastic contributions are equal, has been claimed to relate well to relaxation and consequently, to non-load-associated cracking (D. W. Christensen et al., 2017).

An issue of paramount importance is the compatibility of SBS with the bitumen (Masson et al., 2003), especially when aged PMB is incorporated in new blends. Asphalt production and environmental conditions influence the polymer and the bitumen differently, leading to a degradation of the polymer chains (chain scission) as a result of ageing (Lu & Isacsson, 1998; Yut & Zofka, 2011). A common practice to analyse bitumen composition is the separation into generic fractions according to their polarity, ranging from the more polar asphaltenes to the less polar aromatics, resins and saturates. Researchers have attributed the SBS-degradation phenomenon to the swelling of polymers by the lighter compounds, typically aromatics (Lesueur, 2009). This process contributes to an increase in asphaltenes and subsequently, to a more severe stiffening of the SBS bitumen (Kleiziene et al., 2019).

Previous studies have reached a number of conclusions regarding the ageing mechanisms that evolve in bitumen (Pipintakos et al., 2020). However, the role of polymer presence is yet to be understood. Fourier-transform infrared spectroscopy

(FTIR) offers the possibility to unravel, at least partially, the influence of recycling rate and the degradation severity of the SBS. For that purpose, standard infrared ageing indices can account for the functionality of the rejuvenator and the effect in the polymer-related chemical groups, which are an easy target for oxygen due to the unsaturated double-carbon bonds of the polybutadiene blocks (C. Yan et al., 2018).

Undoubtedly, the assessment of new blends and the role of the polymer in these blends becomes a complex task, given the fact that various mechanisms take place. Previous efforts have shown that rheological and chemical properties are able to track polymer activity and degradation as well as the effectiveness of a rejuvenating agent to restore the ageing properties of PMB-free RA. However, the gap here is that limited studies have addressed the residual effects of RPMB, namely elasticity after degradation when incorporated at various rates. Another important aspect missing is whether a rejuvenator can have an added value into restoring an RPMB.

The focus of this paper is to address the effect of adding RPMB in new binder blends at various replacement rates, and the effect of using a rejuvenator, a typical practice nowadays when PMB-free RA is considered. Besides assessing the effect of recycling rate and use of a rejuvenator, another goal was to evaluate which tests are sensitive to capture changes among the studied blends and more importantly, to capture whether the old polymer is still active and up to which recycling rate. The motivation of this research is a first step into investigating the potential of horizontal recycling (SMA into an SMA) and not downcycling (SMA to an AC base).

Objectives

In this study, blends of RPMB and virgin PMB are rheologically and physicochemically assessed at a binder level. The following objectives were set to address more specific

research questions:

- To investigate the relationship between the recycling rate of reclaimed polymer-modified binder (RPMB) and the performance of blends with virgin polymer modified binder (PMB).
- To explore whether the addition of a bio-based rejuvenator is beneficial to the chemo-rheological properties of the blends.
- To assess the level of polymer activity in blends of RPMB and virgin PMB with and without rejuvenator.

Materials and methods

Binder sources

This study uses an RPMB source and a virgin PMB as primary materials. The RPMB is a modified binder from a single road source, extracted and recovered using trichloroethylene as a solvent according to EN 12697-1:2012. The original properties of the RPMB are not known; however, preliminary FTIR analyses identified SBS-related peaks and thus, the observed peaks can be clearly assigned to SBS presence. The reference binder is a commercially available PMB (type 40/100-75) modified with SBS. Therefore, both RPMB and PMB are SBS-based binders.

Binder blend design

Three binder replacements rates were considered: 20%, 40% and 60% (percentage by mass of total binder blend). Additionally, the virgin PMB and the field-aged binder (100% RPMB) were tested, referred to as REF and 100% RA samples, respectively. The three replacement rates were also treated with a rejuvenator to investigate its influence on the chemo-rheological characteristics of the blends. A rejuvenator

originating from crude tall oil was selected based on its bio-based origin, commercial availability and previous experiences with RPMB. The rejuvenator has a yellow colour and is liquid at room temperature, with a flash point above 280°C and kinematic viscosity of 100 mm²/s at 20°C. Its dosage was determined to achieve a penetration value similar to that of the reference binder. To keep the recycling rates with and without rejuvenator comparable, the amount of rejuvenator was subtracted from the virgin binder quantity. An overview of the composition of the blends is presented in Table 1. The binder blends without rejuvenator were labelled as "replacement rate + RA" and the blends with rejuvenator as "replacement rate + REJ".

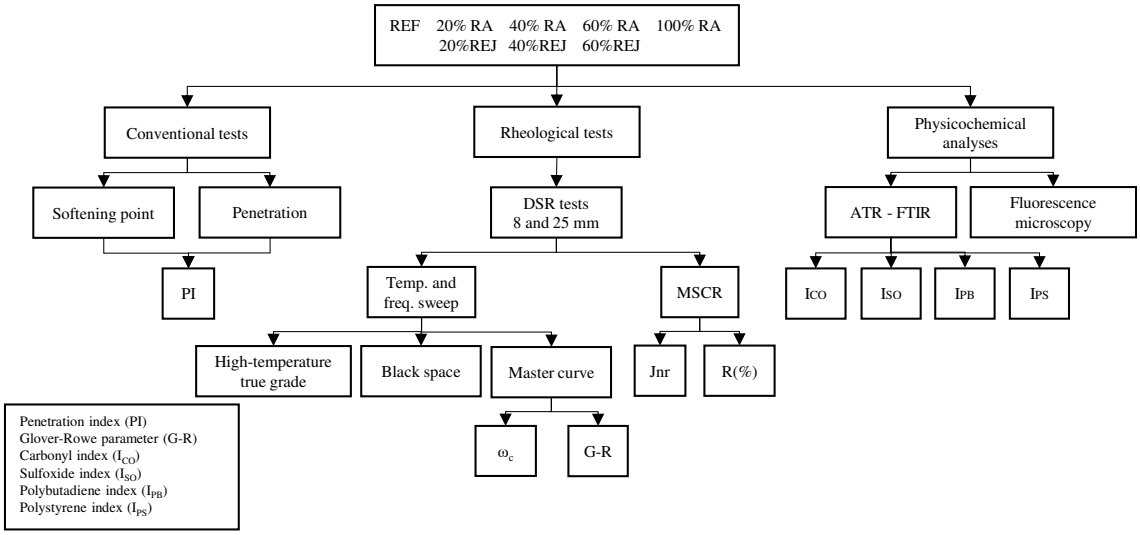
Before blending in batches of 65 grams, the constituent binders were placed in an oven at 170°C for 30 minutes and then stirred separately for 5 minutes on a heating element. The stirring was performed with a low shear mixer and at a speed of 250 min^{-1}. After 15 additional minutes in the oven and 1 minute of stirring, the blends were prepared by adding the correct amounts of RPMB, rejuvenator (at room temperature) and virgin PMB. The final blends were mixed again for 1 minute after another heating period of 5 minutes in the oven.

Table 1: Summary of the blends and their composition (percentage by mass of total binder)

Name	PMB (%)	RPMB (%)	Rejuvenator (%)
REF	100.0	0.0	0.0
20% REJ	78.2	20.0	1.8
40% REJ	56.4	40.0	3.6
60% REJ	34.3	60.0	5.1
20% RA	80.0	20.0	0.0
40% RA	60.0	40.0	0.0
60% RA	40.0	60.0	0.0
100% RA	0.0	100.0	0.0

169 ***Experimental methods***

170 Binder blends were subjected to a suite of tests for performance evaluation. First,
171 conventional tests were carried out on each blend. Then, rheological tests were
172 conducted to evaluate the viscoelastic behaviour and to define certain performance
173 parameters. Finally, physicochemical analyses were performed to assess changes
174 derived from the introduction of RPMB and rejuvenator. The concerning tests and
175 analyses are summarised in Figure 1 and described in the next sections.



176

177 Figure 1: Flowchart of experimental methods

178 ***Conventional tests***

179 Penetration and softening point values were determined according to EN 1426:2015 and
180 EN 1427:2015, respectively. From penetration and softening point values, the
181 penetration index (PI) was calculated to obtain an indication of temperature
182 susceptibility.

183 ***Rheological tests***

184 Rheological properties were assessed using a dynamic shear rheometer (DSR)
185 according to EN 14770:2012. Frequency sweeps were performed utilising an Anton

Paar™ MCR 500 DSR, equipped with an 8 and 25 mm parallel plate geometry in a temperature range from 0°C to 100°C, with steps of 10°C. Frequencies from 1 to 10 Hz were applied in a strain-controlled mode within the linear viscoelastic region of the binder blends. For every blend, two replicates were tested. The results were processed using the RHEA™ software (Abatech, 2011), and the master curves were constructed at a reference temperature of 20°C based on the Christensen-Anderson (CA) model (D. W. J. Christensen & Anderson, 1992). The crossover frequency (ω_c) used in this model is considered the frequency where the viscous and elastic contributions are equal. This parameter is used to evaluate the viscoelastic behaviour of binder blends, and it has also been proposed as a stress relaxation indicator (Jing et al., 2020).

Another commonly used parameter is the Glover-Rowe parameter (G-R), which indicates the susceptibility to non-load-associated cracking. This parameter was calculated using equation (1) with G* and phase angle (δ) at a temperature of 15°C and a frequency of 0.005 rad/s (G. Rowe et al., 2014). Previous studies introduced G-R limits of 180 kPa and 600 kPa to indicate the onset of cracking (warning limit) and extensive block cracking (critical limit), respectively (D. Christensen et al., 2019).

$$G - R = \frac{G^* * (\cos\delta)^2}{\sin\delta} \quad (1)$$

Since PMB is also utilised to improve the characteristics at high service temperatures, the MSCR test was performed to assess the binder resistance to permanent deformation. The MSCR test was performed according to EN 16659:2016 in the 25 mm geometry of the DSR at 50°C. This temperature was selected since it corresponds to the rutting test temperature in the Flemish region (Agentschap Wegen en Verkeer, 2019). The main parameters extracted from this test are the average recovery percentages (R_{100} and R_{3200}), which indicate the recoverable shear strain, and the non-

210 recoverable creep compliances ($J_{nr,100}$ and $J_{nr,3200}$), which are the unrecovered shear
211 strains divided by the applied shear stresses. They are calculated at shear stress levels of
212 100 Pa and 3200 Pa.

213 ***Physicochemical analyses***

214 The attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)
215 analysis method is a technique that uses infrared light to observe changes in chemical
216 bonds. In this study, the test was performed taking 32 repetitive scans on a binder
217 sample using a Thermo Fisher Scientific Nicolet iS™ 10 spectrometer. The scans were
218 performed with a resolution of 4 cm^{-1} in a range between 4000 cm^{-1} and 400 cm^{-1}. The
219 average of the 32 scans yields a spectrum that is normalised before analysis. The
220 normalisation procedure is based on the methods described in previous studies (Hofko
221 et al., 2018; Margaritis et al., 2020): first, the spectra are shifted to an absorbance of 0 at
222 1753 cm^{-1}. Then, the spectra are scaled to an absorbance of 1 at 2923 cm^{-1}.
223 The analysis of the spectra allows the identification of chemical bonds present in
224 the material. To assess the ageing state of the binders, the carbonyl and sulfoxide areas
225 are generally considered as effective indicators (Marsac et al., 2014). Also, traces of
226 modification with SBS can be captured around two distinctive peaks: one at 966 cm^{-1}
227 (polybutadiene area) and another one at 699 cm^{-1} (polystyrene area). The calculation of
228 the indices is performed by dividing the integration of the area over the integration of a
229 reference area. The areas were integrated using the tangential valley-to-valley approach.
230 A reference area that is stable during ageing, the aliphatic group (Lamontagne et al.,
231 2001), is used in this study.
232 It must be noted here that the carbonyl group is typically defined in the range of
233 1655-1760 cm^{-1}, representing mostly the formation of ketones (Lamontagne et al., 2001;

234 Petersen & Glaser, 2011). However, the rejuvenator used shows a peak around 1740
235 cm^{-1}, corresponding to carbonyl esters, which hinders the accurate integration of the
236 carbonyl area. To avoid possible overestimation of the carbonyl index due to the
237 rejuvenator presence, the baseline limit of the carbonyl group was set between 1655 and
238 1720 cm^{-1}. All the considered indices and their limits are presented in Table 2.

239 Table 2: Functional groups, baseline limits and their corresponding indices

Functional group	Baseline limits (cm^{-1})	Index
Aliphatic group (A_{ref})	1350-1395 + 1395-1515	
Carbonyl group (A_{CO})	1655-1720	$I_{CO} = A_{CO}/A_{ref}$
Sulfoxide group (A_{SO})	986-1047	$I_{SO} = A_{SO}/A_{ref}$
Polybutadiene group (A_{PB})	960-970	$I_{PB} = A_{PB}/A_{ref}$
Polystyrene group (A_{PS})	695-705	$I_{PS} = A_{PS}/A_{ref}$

240 Since compatibility between the different components of the blends is crucial,
241 microscopic images were captured using fluorescence microscopy to observe the
242 morphology of binder blends. The microscope is a Carl Zeiss Axioskop 40Fl with an
243 HBO 50 light source, while a deltapix DP200 digital camera is used to capture the
244 images. Different protocols have been suggested to investigate PMB using fluorescence
245 microscopy (Kou et al., 2019). The thin-film method is selected for sample preparation
246 in this study to investigate storage stability. First, the binder blends were homogenised,
247 and then a hot drop of the blend was placed between two glass plates, resulting in a thin
248 layer of bitumen. Next, the sample was isothermally stored for 30 minutes at 160°C.
249 Then, the samples were immediately inspected with the microscope. Due to the thin
250 sample size, the sample cooled down rather quickly during the test.

251 **Results and discussion**

252 ***Conventional tests***

253 The results of the conventional tests are presented in Table 3. The effect of the polymer
254 modification in the reference PMB can be clearly observed by the high softening point

and PI. The 100% RPMB sample seemed heavily aged, with a penetration value of 10 x 0.1 mm. Due to the relatively moderate softening point of this binder, the PI is negative, which indicates that the residual effect of polymer modification is relatively small. Note that a negative PI can also be interpreted as a sign of non-modified binder. Thus, RPMB exhibited signs of severe polymer degradation.

Table 3: Penetration, softening point and penetration index of the blends

	REF	20% REJ	40% REJ	60% REJ	20% RA	40% RA	60% RA	100% RA
Penetration (0.1mm)	51	52	52	53	46	28	25	10
Softening point (°C)	76.4	69.8	52.6	53.6	70.4	61.0	63.2	68.6
Penetration index	3.84	2.89	-0.46	-0.20	2.65	-0.06	0.08	-0.48

As expected, the non-rejuvenated blends (20% RA, 40% RA and 60% RA) showed a decrease in penetration value with increasing RA content. However, the evolution of the softening point is less obvious. Above 20% RA, there is a remarkable drop in softening point below the values of the two constituent binders. This phenomenon might be caused by the dilution of the polymer content in the blend due to the high RA binder content, which appeared to contain inactive polymers. At a recycling rate of 60%, the softening point slightly increased again because of the higher percentage of aged binder. Due to the relationship between softening point and PI, the same trend was observed in PI values.

The penetration values of the rejuvenated blends were similar to that of the reference binder, as intended in the experiment design. The softening point followed a similar trend as their non-rejuvenated counterparts: a relatively high value for the 20% recycling rate, the lowest value at 40%, and a slight increase for the 60% recycling rate. Due to the softening effect of the rejuvenator, the softening points at high recycling rates dropped significantly compared to the non-rejuvenated blends.

Rheological characterisation

High-temperature true grade

The high-temperature true grade is used to investigate the performance of the blends at temperatures where the polymer is more likely to be active. The high-temperature true grade of the non-rejuvenated blends increased alongside the increase in recycling rate, as shown in Figure 2. The increasing trend substantiates the stiffening effect of adding RA, which was also observed from conventional properties. Conversely, the addition of rejuvenator caused a softening effect, leading to lower true grade values. All rejuvenated blends yielded similar values, which agrees with the trend observed in binder penetration.

The softening point and the high-temperature true grade show a different trend. The softening point seemed to be more susceptible to the presence of virgin polymer, whereas the true grade was mainly driven by binder hardening.

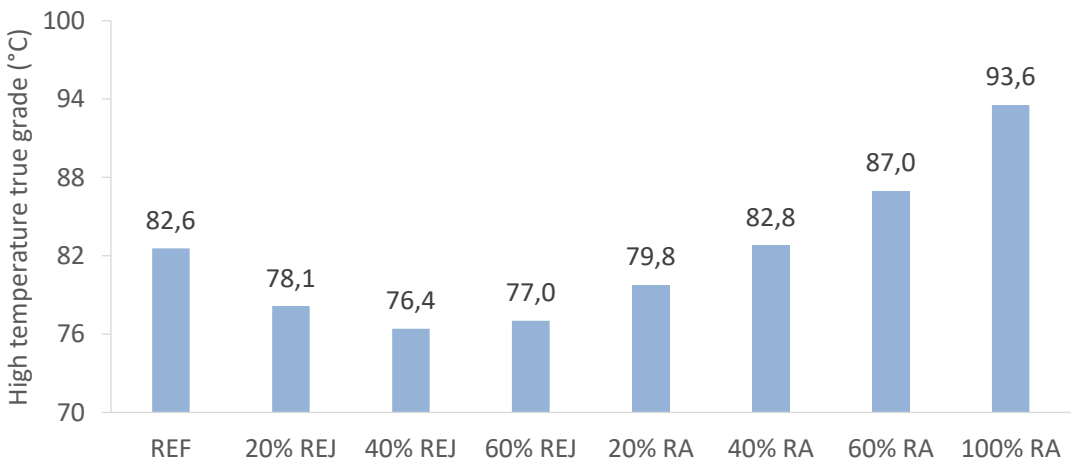


Figure 2: Bar chart of the high-temperature true grade of blends

Master curve

Figure 3 and Figure 4 show the master curve averages for complex modulus and phase angle, respectively. All measurements were within the precision described in EN

14770:2012, namely below 10% and 5% for G* and delta, respectively. The root-mean-square error of the fitted CA models ranged between 3.64% and 6.95%, and the R^2 was above 98.9% for all binder blends.

Complex modulus results ranged from the lowest values, exhibited by the reference binder, to the highest values exhibited by the recovered RPMB. The addition of RPMB increased the complex modulus of the blends without rejuvenator at all frequencies. However, the three blends with rejuvenator exhibited a similar complex modulus throughout the range of frequencies despite the different recycling content. This means that the rejuvenator content determined to target the same penetration value yielded blends of similar stiffness over the entire frequency range.

As illustrated in Figure 4, the reference binder displayed multiple phase angle values around 1.E-05 rad/s most likely due to segregation of the polymer. This segregation can be the result of non-isothermal cooling or slow heating, as concluded by Soenen et al. (Soenen et al., 2008). Note also that the reference binder exhibited a plateau between 1 rad/s and 1.E-03 rad/s, and even a slight decrease in phase angle at frequencies below 1.E-03 rad/s (equivalent to the response at high temperatures), as expected from the more elastic response of PMB. This effect known in the literature as 'feathering' occurs when a polymer is present and active (Mensching et al., 2016). Similarly, blends with 20% RAB (with and without rejuvenator) showed an attempt to maintain the phase angle at lower frequencies, which indicates a certain level of polymer activity. Conversely, blends with 40% RAB and above showed a continuous decrease in phase angle with increasing frequency, which is characteristic of binders with no polymer or negligible polymer response. For frequencies above 0.1 rad/s, all blends with rejuvenators yielded almost the same phase angle, which was higher than that of blends without rejuvenator, indicating the presence of a rejuvenator increased the

viscous response and higher frequencies. This may be indicative of a better ability to relax stresses at lower temperatures.

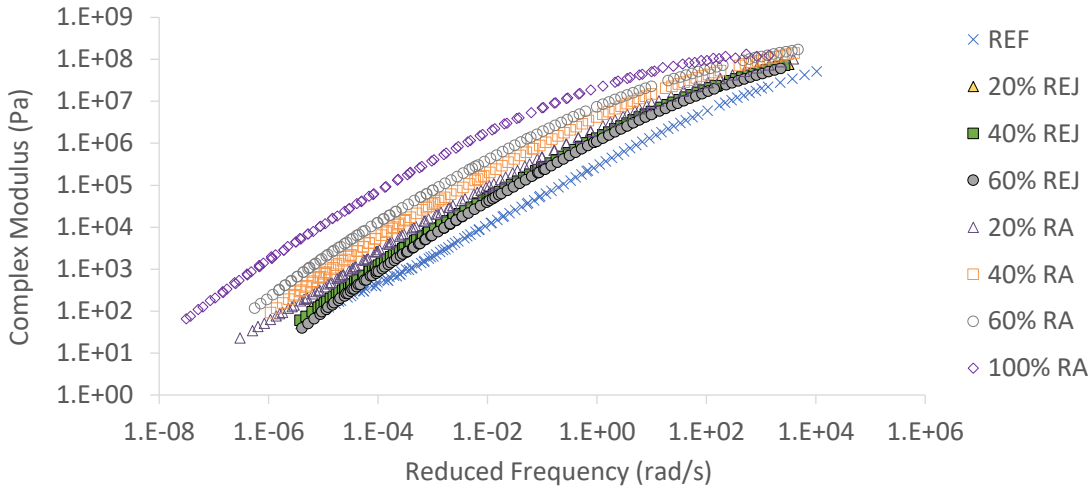


Figure 3: Complex modulus master curves of the binders

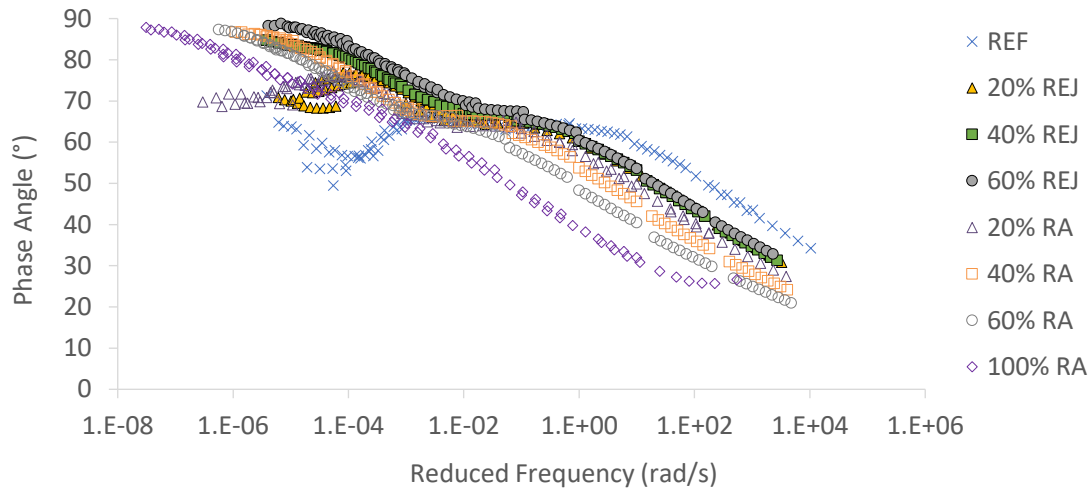


Figure 4: Phase angle master curves of the binders

Black curve

Figure 5 illustrates the black curve of the eight binders in complex modulus-phase angle space. All binders exhibited a similar response for complex modulus above 1E+05 Pa, which corresponds to the intermediate- and low-temperature range. Below 1E+05 Pa, the reference binder showed a relatively constant phase angle, followed by a reduction

and a slight increase. This characteristic response of PMB binders, known as 'curling', substantiated the presence of polymer in the virgin PMB. The two blends with 20% RPMB, which yielded a plateau in phase angle at low reduced frequencies, also showed signs of polymer activity. Out of the remaining binder samples, only that with 40% RPMB and rejuvenator exhibited a minimal sign of polymer response. Based on black curve results, the addition of the rejuvenator did not noticeably restore the elasticity of the blends with RPMB. The 100% RA sample does not show any remaining polymer activity, which agrees with a previous study on field aged binders (Margaritis et al., 2020).

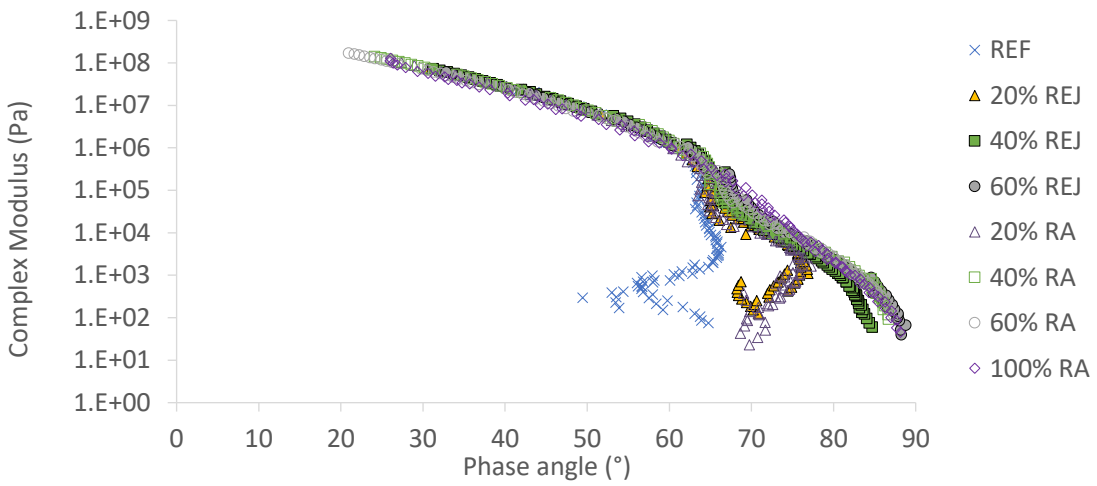


Figure 5: Black diagram of the binder blends.

Multiple stress creep-recovery test

Table 4 confirms the findings from phase angle and black curve: the reference binder and both blends with 20% RPMB exhibited low non-recoverable compliance and high strain recovery (above 90%), which is characteristic of polymer activity. Above 20% RPMB, the blends experienced a 50% drop in strain recovery and, potentially, greater susceptibility to permanent deformation at higher temperatures. The softening effect of the rejuvenator tended to make the blends more compliant and less elastic (lower strain

recovery), particularly at 60% RPMB.

Table 4: Penetration, softening point and penetration index of the blends

	REF	20% REJ	40% REJ	60% REJ	20% RA	40% RA	60% RA	100% RA
$J_{nr,100Pa}$ (kPa^{-1})	0.02	0.05	0.27	0.50	0.05	0.11	0.06	0.02
$J_{nr,3200\ Pa}$ (kPa^{-1})	0.01	0.02	0.26	0.56	0.02	0.11	0.06	0.01
R_{100} (Pa)	93.4%	92.5%	53.1%	24.6%	91.9%	44.2%	45.0%	56.3%
R_{3200} (Pa)	96.2%	94.2%	49.7%	14.3%	94.3%	40.4%	43.8%	57.0%

Crossover frequency

The crossover frequency is given in Figure 6 for the different recycling rates, with and without rejuvenator. The non-rejuvenated blends show a gradual, almost linear decrease with increasing RPMB content, which can be interpreted as a decline in the viscous component. A reduction in the viscous component reduces the ability to relax stresses, which may increase the susceptibility to low-temperature cracking (D. W. Christensen et al., 2017; Jing et al., 2020; G. M. Rowe & Sharrock, 2016). Conversely, the crossover frequency remained relatively constant for the rejuvenated blends. This means the rejuvenator compensated for the stiffening effect of increasing recycling rate and kept the balance between the elastic and viscous components. As a result, the addition of the rejuvenator seems to have a positive effect on the ability to relax stresses at low temperatures. The results of this study are in line with previous investigations on non-modified RAB blends. Previous studies indicated that both ageing and an increase in recycling rate decreased the crossover frequency (Gómez-Meijide et al., 2018), whereas the opposite effect happened with the addition of rejuvenators (Dhasmana et al., 2019).

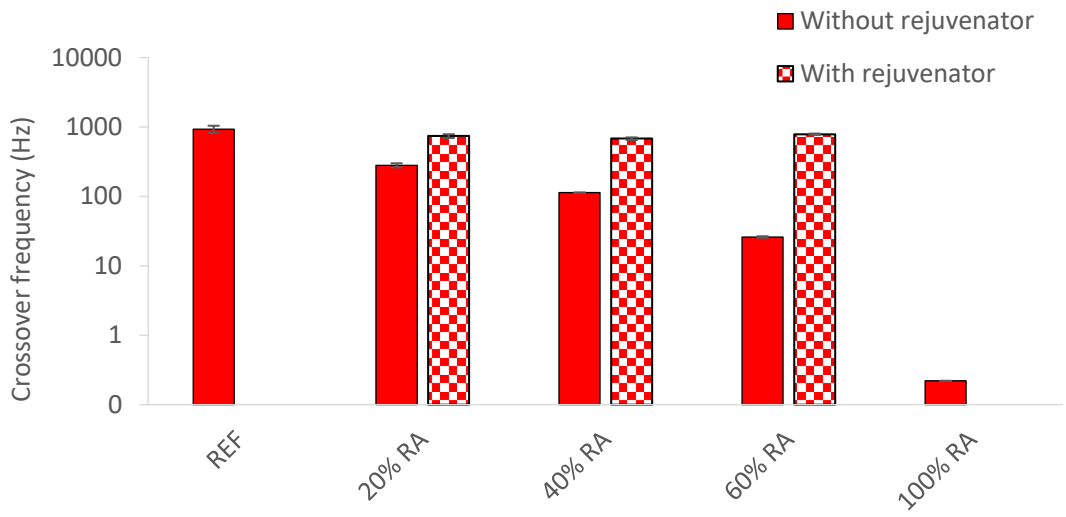


Figure 6: Evolution of crossover frequency with increasing recycling rate, with and without rejuvenator.

Glover-Rowe parameter

G-R values and damage thresholds are depicted in a black space diagram in Figure 7. All blends fell in the no damage region apart from the 100% RA; the level of field ageing experienced by this binder made it prone to damage. For the non-rejuvenated blends, the G-R parameter shifted up to the left. This observation confirms that both ageing and increasing recycling rate result in a higher susceptibility to cracking. Furthermore, all rejuvenated blends provided G-R values similar to that of of the reference binder, with the difference being a slight increase in phase angle with increasing RPMB content. Both G-R and crossover frequency results proved that the addition of this rejuvenator was beneficial in terms of non-load-associated cracking.

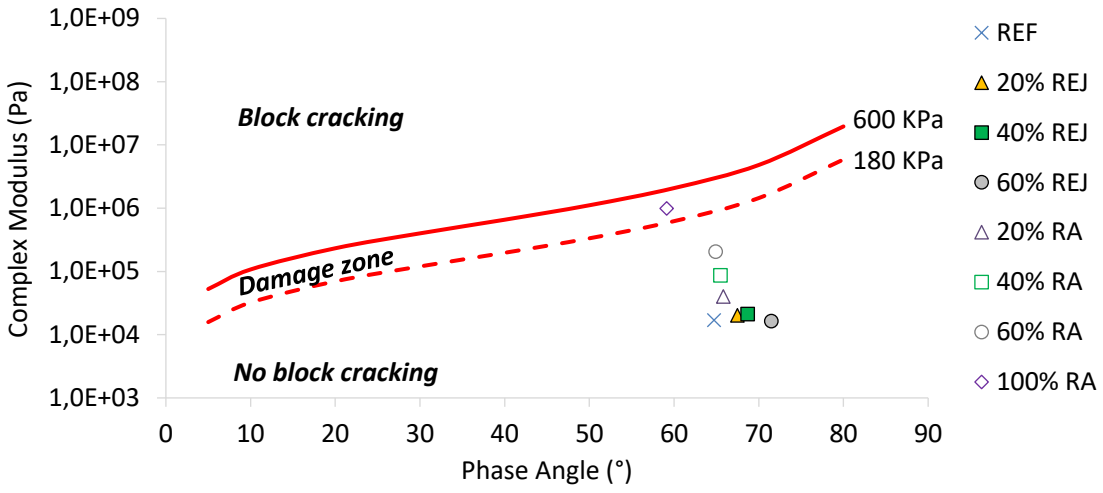


Figure 7: Glover-Rowe parameters plotted with the limit thresholds in a black space diagram

Physicochemical characterisation

FTIR spectroscopy

The sulfoxide and carbonyl indices were calculated to examine ageing level, whereas the polybutadiene and polystyrene indices were used as polymer-related indices. The calculated sulfoxide indices are presented in Figure 8. This study found an increasing trend in sulfoxide indices with increasing recycling rate. As depicted in Figure 8 the increase in recycling rate resulted in an almost linear increase for both blends, with and without rejuvenator.

The inclusion of rejuvenator at lower recycling rates (20% and 40%) did not have a substantial effect. On the other hand, a decrease in the sulfoxide index is observed for the 60% RPMB sample. In fact, an increase in polarity is accompanied by the formation of sulfoxide-related moieties, possibly present in the more polar fractions such as asphaltenes. The addition of rejuvenator is expected to increase the maltene fraction and, consequently, to proportionally reduce the asphaltene component. The expected increase in total sulfoxide groups associated with ageing can be visualised in

Figure 8 as a result of the further addition of aged RPMB. Consequently, the reduction in the sulfoxide index is linked to the increasing dosage of rejuvenator, especially noticeable on the 60% RA blend (Figure 8). From these results, it can be assumed that the use of rejuvenator, especially at a higher dosage, can be regarded as beneficial in terms of ageing, especially at higher recycling rates.

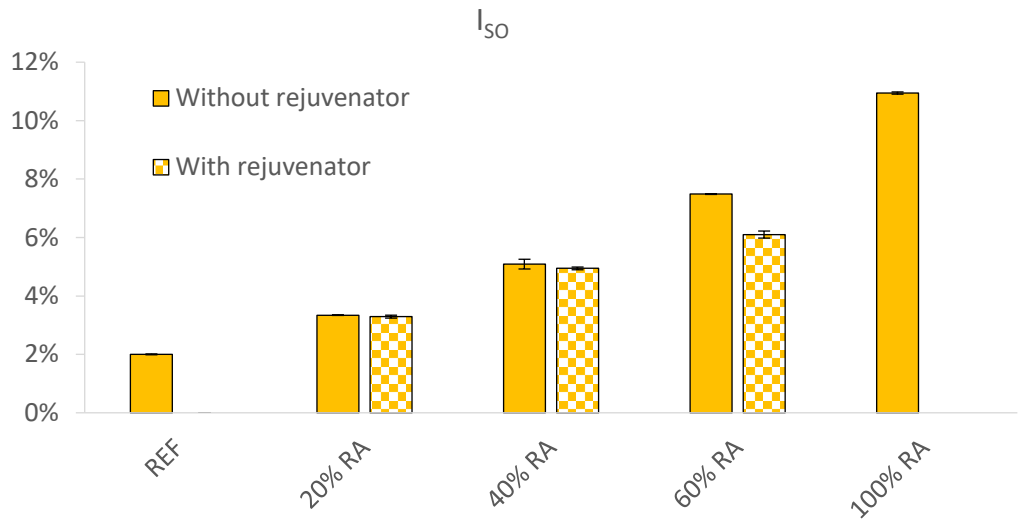
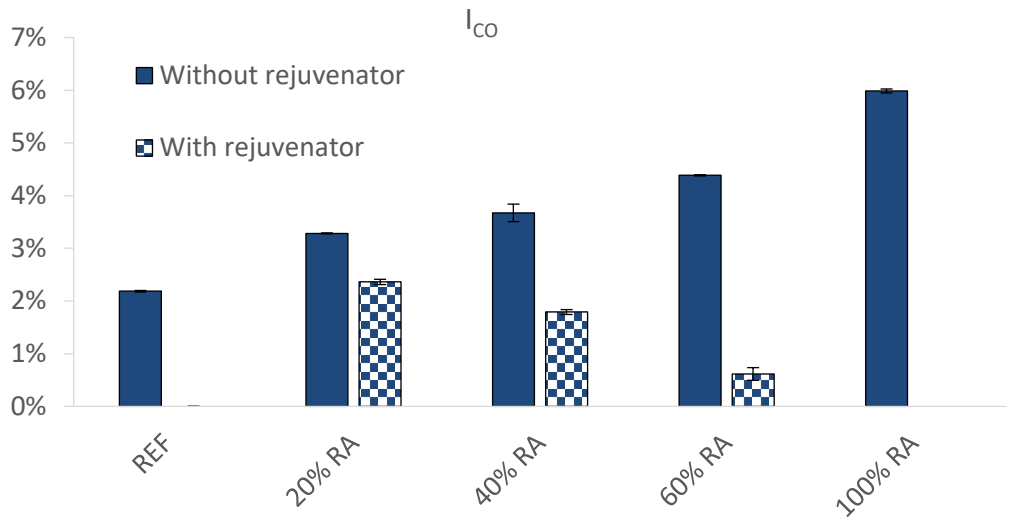


Figure 8: Evolution of sulfoxide index with increasing recycling rate and with rejuvenator presence.

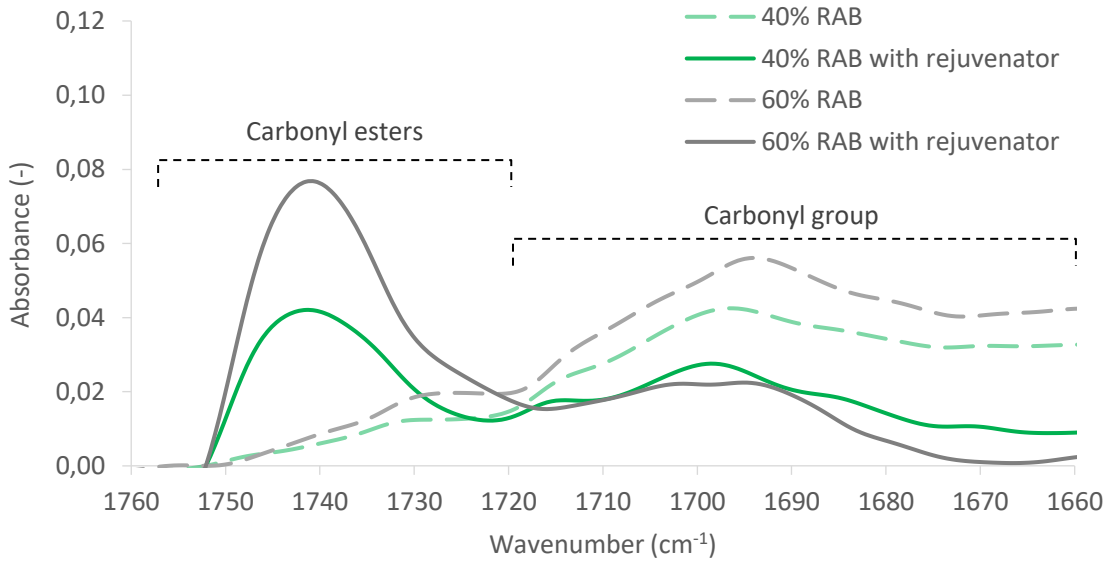
Similarly to the sulfoxide index, the carbonyl index (depicted in Figure 9) increased almost linearly with the increase in recycling rate, an observation now only valid for the non-rejuvenated samples. Conversely, the inclusion of rejuvenator led to a decrease in the carbonyl index. A more in-depth inspection of the actual spectra, given in Figure 10, revealed an overlap between the peaks of the carbonyl esters group (1700-1760 cm^{-1}) corresponding to the rejuvenator, and the carbonyl group (1655-1760 cm^{-1}) coming from the aged binder, an issue already discussed in the methods section. The rise in rejuvenator dosage led to a decrease in the absolute absorbance value around 1700 cm^{-1}, and that may indicate a partial restoration effect. However, considering the area integration, part of the carbonyl group is not encountered when considering a

414 narrower band (1655-1720 instead of 1655-1760 cm^{-1}), which led to an underestimation
415 of the carbonyl index. However, consideration of a wider band would have led to an
416 overestimation of the carbonyl index due to carbonyl ester peak. Consequently, it can be
417 concluded that the assessment of the carbonyl index in blends with rejuvenator is
418 considered problematic.



419

420 Figure 9: Evolution of carbonyl index with increasing recycling rate and with
421 rejuvenator presence.



422

423 Figure 10: FTIR spectra of the overlapping peaks of carbonyl and rejuvenator

For a critical assessment of the degradation level of the SBS polymer, the two indices responsible for this phenomenon (I_{PS} and I_{PB}) were utilised. Since the ultimate goal was to reflect the degradation level of the polymer, a cumulative polymer index, i.e. the sum of polystyrene (I_{PS}) and polybutadiene (I_{PB}), was employed here. From the previous FTIR analysis, it becomes apparent that the carbonyl index will not depict the actual ageing severity accurately when rejuvenators, like the one considered in this study, are included in the blend. For that reason, the sulfoxide index (I_{SO}) is regarded as the most appropriate value to evaluate ageing severity, from a chemical perspective, for all the blends in this study. A comparative plot of the cumulative polymer index and the I_{SO} allows for a quantification of polymer degradation (Figure 11).

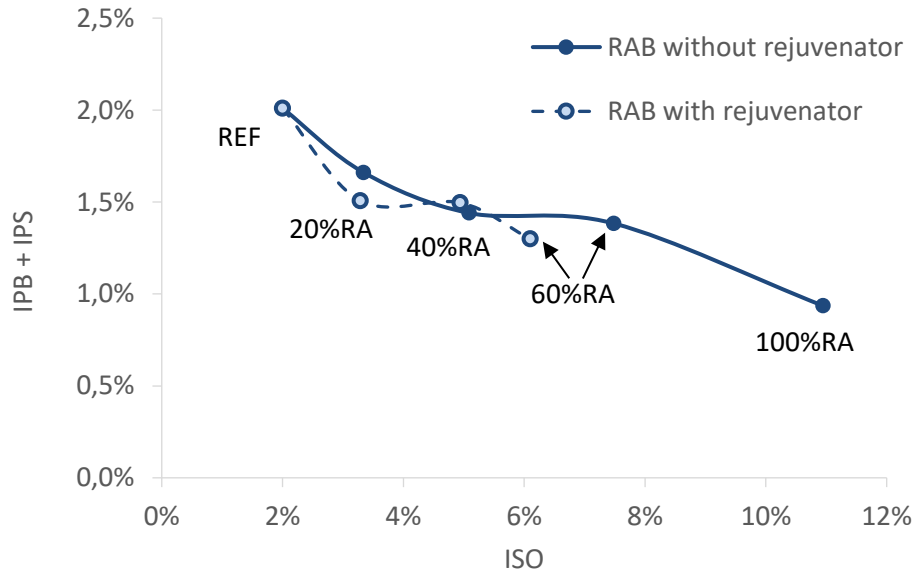


Figure 11: Cumulative polymer index versus ageing index for different recycling rates

The overall trend is a simultaneous decrease in the cumulative polymer index and the sulfoxide index with increasing recycling rate. The reduction in cumulative polymer index indicates scission of polymer chains. It can be concluded that the inclusion of RPMB has a similar effect as bitumen ageing. In terms of polymer restoration, the rejuvenator appears to not improve the RPMB at 20% recycling rate

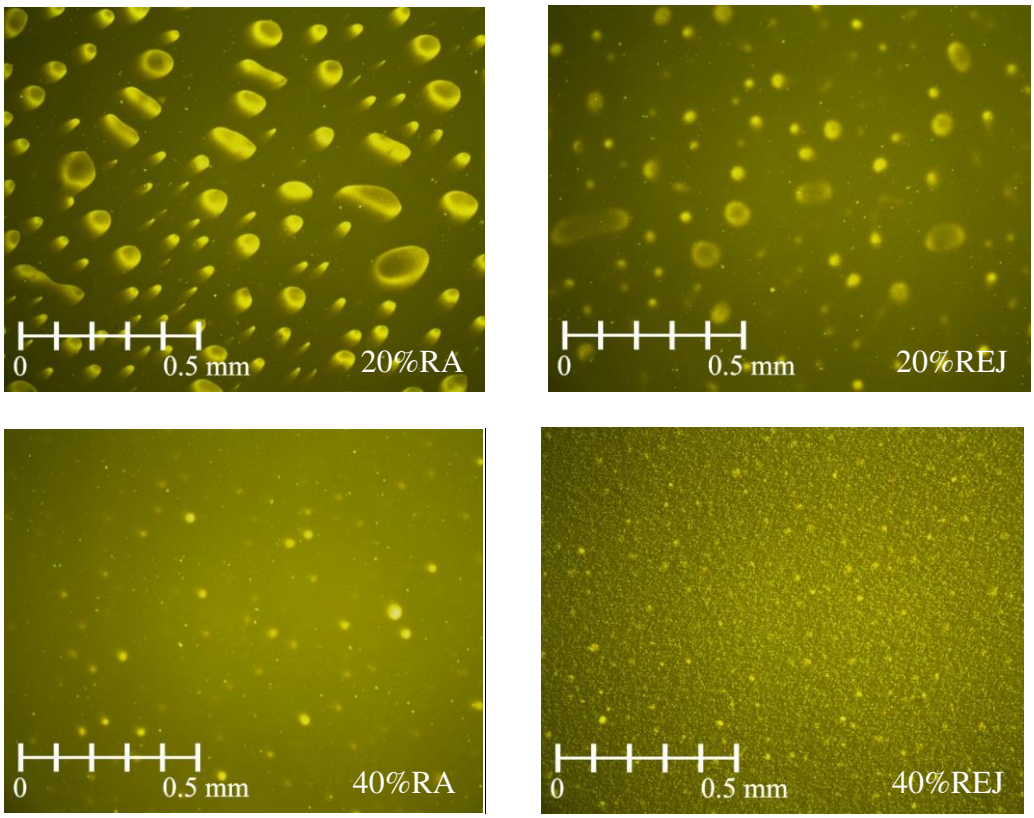
441 compared to the same non-rejuvenated blend, while similar ageing severity is observed
442 for this recycling rate. This finding might be an indication that the rejuvenator has an
443 adverse effect on the compatibility of the virgin PMB with the RPMB. Conversely, the
444 addition of rejuvenator appeared to be beneficial up to 40%, as indicated by the plateau
445 in Figure 11 (polymer degradation remained somehow stable). More specifically, these
446 plateaus seem to range between 20 and 40% RA when adding rejuvenator and between
447 40 and 60% RA without rejuvenator. For 40% and 60% RA, the rejuvenator appears to
448 have little effect on polymer restoration compared to the blends without rejuvenator.
449 Among the evaluated blends with and without rejuvenator, polymer degradation is most
450 evident for a recycling rate of 60%.

451 *Fluorescence microscopy*

452 It is also critical to assess the impact of the recycling rate and rejuvenator on bitumen
453 morphology. The findings from the FTIR analysis indicated that rejuvenated blends
454 with 20% and 40% RPMB exhibited a similar level of polymer degradation despite the
455 increased aged RPMB content of the latter. Thus, the focus of the microscopic
456 investigation is exclusively on these two recycling rates to better understand the
457 influence that the rejuvenator may have on the polymer phase. The microscopic images
458 are depicted in Figure 12. It appeared that the increase in RPMB content led to a
459 shrinkage and a total reduction in the polymer-rich phase for blends with and without
460 rejuvenator (Figure 12).

461 The impact of the rejuvenator on blend morphology is depicted on the right side
462 of Figure 12. For 20% RPMB, the number and size of polymer particles was found to
463 decrease, which may have an association with the compatibility between the
464 compounds. For 40% RPMB, the number of round polymer particles seemed to increase

465 for the rejuvenated blend, although their size appears smaller. The reason for these
466 changes in bitumen morphology is still an open question that requires further
467 investigation on SBS compatibility in the new blend as well as on the compatibility of
468 the rejuvenator in the blends.

469 

470

471 Figure 12: Fluorescence images (x100) of selected recycling rates and the effect of
472 rejuvenator

473 **Conclusions and recommendations**

474 A chemo-rheological investigation was performed on blends of virgin PMB with 0%,
475 20%, 40%, 60% and 100% of reclaimed PMB (RPMB), recovered from an actual
476 surface layer mixture. Additionally, rejuvenated blends were produced for the 20%,
477 40% and 60% recycling rates by adding a bio-based, tall oil rejuvenator. The following
478 findings were made:

479 - Even though the presence of SBS polymer in RPMB was verified with FTIR, all

tests showed severe polymer degradation and no signs of residual polymer activity in the recovered binder, especially noticeable for the 60% and 100% recycling rates. Furthermore, the recovered binder exhibited high susceptibility to non-load-associated cracking according to the Glower-Rowe parameter. This is a key finding for recycling aged PMB in new asphalt mixtures.

- Polymer dilution lowered the softening point at recycling rates of 20% and 40% whereas an increase in softening point was observed at 60% due to the high content of hard, aged binder. The softening point seemed to be more susceptible to the presence of virgin polymer, whereas the high-temperature true grade was mainly driven by binder hardening.
- Using a fixed target penetration to dose the rejuvenator led to blends with similar high-temperature true grade and master curves. This is not necessarily intuitive since binder penetration is measured at 25°C, high-temperature true grade is defined by a fixed stiffness and phase angle, and master curves are obtained over a range of temperatures and frequencies.
- The carbonyl index, frequently used as an indication of binder ageing level, may be influenced by the presence of carbonyl esters in the rejuvenator. Therefore, the use of a carbonyl index that accounts only for the carbonyl present, by considering a narrower wavelength range between 1655-1720 cm^{-1}, is highly recommended.

The following conclusions can be drawn from the results of this investigation:

- In addition to the known stiffening effect, the addition of RPMB increased the susceptibility of the blends to non-load-associated cracking as evidenced by the crossover frequency and Glover-Rowe parameter. Furthermore, fluorescence

microscopy revealed that adding RPMB reduced the polymer-rich phase of the blends due to the lack of activity of the polymer present in RPMB.

- The rejuvenator used in this study did not activate or increase the level of activity of the aged polymer present in RPMB. However, this rejuvenator successfully compensated for the stiffening effect of the aged binder and reduced the susceptibility to non-load-associated cracking to levels comparable to those of the virgin PMB binder.
- Several rheological test results (phase angle master curve, black curve, and MSCR) confirmed the characteristic 'feathering' and 'curling' effects associated with active polymer presence on blends up to 20% RPMB for the used materials. The blend with 40% RPMB and rejuvenator showed minimal polymer activity in the black curve and MSCR test. All other blends performed as non-polymer-modified binders.

This study describes a first attempt to recycle RPMB in new premium surface layers by investigating the effect of using an RPMB source and exploring which tests can be useful to capture the possible residual activity of the aged polymer on binder scale. Future work is necessary to further assess the potential of recycling PMB by upscaling the experimental procedure, going from a binder level to a mixture level. This will also allow to better capture the actual degree of blending instead of the full blending scenario of binder testing. Finally, additional tests such as low-temperature cracking should also be performed in a future study. This knowledge is of paramount importance to allow recycling in premium asphalt surfaces and stop downcycling high-quality RAP containing aged PMB milled from surface layers.

Disclosure statement

The authors reported no potential conflict of interest.

Acknowledgements

The authors would like to acknowledge Hilde Soenen from Nynas NV for her assistance on the fluorescence microscopy and her valuable comments. Also, Koen Deckers from BAM Contractors for providing the RA material.

References

Abatech. (2011). *RHEA-Rheology Analysis Software, version 2.3* (

Agentschap Wegen en Verkeer. (2019). *Standaardbestek 250 voor de wegenbouw - versie 4.1.* (

Airey, G. D. (2003). Rheological properties of styrene butadiene styrene polymer modified road bitumens. *Fuel*, *82*(14), 1709-1719. https://doi.org/https://doi.org/10.1016/S0016-2361(03)00146-7

Anthonissen, J., Van den bergh, W., & Braet, J. (2016). Review and environmental impact assessment of green technologies for base courses in bituminous pavements. *Environmental Impact Assessment Review*, *60*, 139-147. https://doi.org/https://doi.org/10.1016/j.eiar.2016.04.005

Aurangzeb, Q., Al-Qadi, I. L., Ozer, H., & Yang, R. (2014). Hybrid life cycle assessment for asphalt mixtures with high RAP content. *Resources, Conservation and Recycling*, *83*, 77-86. https://doi.org/https://doi.org/10.1016/j.resconrec.2013.12.004

Bajaj, A., Epps Martin, A., King, G., Glover, C., Kaseer, F., & Arámbula-Mercado, E. (2020). Evaluation and classification of recycling agents for asphalt binders. *Construction and Building Materials*, *260*, 119864. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2020.119864

Christensen, D., Mensching, D., Rowe, G., Anderson, R. M., Hanz, A., Reinke, G., & Anderson, D. (2019). *Past, Present, and Future of Asphalt Binder Rheological Parameters: Synopsis of 2017 Technical Session 307*. 96th Annual Meeting of the Transportation Research Board.

Christensen, D. W., Anderson, D. A., & Rowe, G. M. (2017). Relaxation spectra of asphalt binders and the Christensen–Anderson rheological model. *Road Materials and Pavement Design*, *18*(sup1), 382-403. https://doi.org/10.1080/14680629.2016.1267448

Christensen, D. W. J., & Anderson, D. A. (1992). Interpretation of dynamic mechanical test data for paving grade asphalt (*Asphalt Paving Technology: Association of Asphalt Paving Technologists-Proceedings of the Technical Sessions*.

D'Angelo, J., Kluttz, R., Dongre, R. N., Stephens, K., & Zanzotto, L. (2007). Revision of the superpave high temperature binder specification: the multiple stress creep recovery test (with discussion). *Journal of the Association of Asphalt Paving Technologists*, *76*.

Dhasmana, H., Hossain, K., & Karakas, A. S. (2019). Effect of long-term ageing on the rheological properties of rejuvenated asphalt binder. *Road Materials and Pavement Design*, 1-19. https://doi.org/10.1080/14680629.2019.1686051

Domingos, M. D. I., & Faxina, A. L. (2016). Susceptibility of Asphalt Binders to Rutting: Literature Review. *Journal of Materials in Civil Engineering*, *28*(2). https://doi.org/https://doi:10.1061/(ASCE)MT.1943-5533.0001364

Garcia Cucalon, L., Kaseer, F., Arámbula-Mercado, E., Epps Martin, A., Morian, N., Pournoman, S., & Hajj, E. (2019). The crossover temperature: significance and application towards engineering balanced recycled binder blends. *Road Materials and Pavement Design*, *20*(6), 1391-1412. https://doi.org/https://doi.org/10.1080/14680629.2018.1447504

Gómez-Meijide, B., Ajam, H., Lastra-González, P., & Garcia, A. (2018). Effect of ageing and RAP content on the induction healing properties of asphalt mixtures. *Construction and Building Materials*, *179*, 468-476. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2018.05.121

Hofko, B., Porot, L., Falchetto Cannone, A., Poulikakos, L., Huber, L., Lu, X., Mollenhauer, K., & Grothe, H. (2018). FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. *Materials and Structures*, *51*(2), 45. https://doi.org/https://doi.org/10.1617/s11527-018-1170-7

Jacobs, G., Margaritis, A., Hernando, D., He, L., Blom, J., & Van den bergh, W. (2021). Influence of soft binder and rejuvenator on the mechanical and chemical properties of bituminous binders. *Journal of Cleaner Production*, *287*. https://doi.org/10.1016/j.jclepro.2020.125596

Jing, R., Varveri, A., Liu, X., Scarpas, A., & Erkens, S. (2020). Rheological, fatigue and relaxation properties of aged bitumen. *International Journal of Pavement Engineering*, *21*(8), 1024-1033. https://doi.org/10.1080/10298436.2019.1654609

Kleiziene, R., Panasenkiene, M., & Vaitkus, A. (2019). Effect of Aging on Chemical Composition and Rheological Properties of Neat and Modified Bitumen. *Materials (Basel)*, *12*(24). https://doi.org/10.3390/ma12244066

Kodippily, S., Holleran, G., & Henning, T. F. P. (2017). Deformation and cracking performance of recycled asphalt paving mixes containing polymer-modified binder. *Road Materials and Pavement Design*, *18*(2), 425-439. https://doi.org/10.1080/14680629.2016.1181559

Kou, C., Xiao, P., Kang, A., Mikhailenko, P., Baaj, H., & Wu, Z. (2019). Protocol for the morphology analysis of SBS polymer modified bitumen images obtained by using fluorescent microscopy. *International Journal of Pavement Engineering*, *20*(5), 585-591. https://doi.org/10.1080/10298436.2017.1316647

Lamontagne, J., Dumas, P., Mouillet, V., & Kister, J. (2001). Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens. *Fuel*, *80*(4), 483-488. https://doi.org/https://doi.org/10.1016/S0016-2361(00)00121-6

Lesueur, D. (2009). The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, *145*(1), 42-82. https://doi.org/https://doi.org/10.1016/j.cis.2008.08.011

Liu, G., Nielsen, E., Komacka, J., Leegwater, G., & van de Ven, M. (2015). Influence of soft bitumens on the chemical and rheological properties of reclaimed polymer-modified binders from the “old” surface-layer asphalt. *Construction and Building Materials*, *79*, 129-135. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2015.01.002

Lu, X., & Isacsson, U. (1998). Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens. *Fuel*, *77*(9), 961-972. https://doi.org/https://doi.org/10.1016/S0016-2361(97)00283-4

Margaritis, A., Soenen, H., Fransen, E., Pipintakos, G., Jacobs, G., Blom, J., & Van den bergh, W. (2020). Identification of ageing state clusters of reclaimed asphalt binders using principal component analysis (PCA) and hierarchical cluster

analysis (HCA) based on chemo-rheological parameters. *Construction and Building Materials*, *244*, 118276. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2020.118276

Marsac, P., Piérard, N., Porot, L., Van den bergh, W., Grenfell, J., Mouillet, V., Pouget, S., Besamusca, J., Farcas, F., Gabet, T., & Hugener, M. (2014). Potential and limits of FTIR methods for reclaimed asphalt characterisation [journal article]. *Materials and Structures*, *47*(8), 1273-1286. https://doi.org/https://doi.org/10.1617/s11527-014-0248-0

Masson, J., Collins, P., Robertson, G., Woods, J., Margeson, J. J. E., & Fuels. (2003). Thermodynamics, phase diagrams, and stability of bitumen− polymer blends. *17*(3), 714-724.

Mensching, D. J., Gibson, N. H., Andriescu, A., Rowe, G. M., & Sias, J. E. (2016). *Assessing the Applicability of Rheological Parameters to Evaluate Modified Binders*. International Society for Asphalt Pavements Symposium and 53rd Petersen Asphalt Research Conference, Jackson Hole, Wyoming.

Petersen, J. C., & Glaser, R. (2011). Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. *Road Materials and Pavement Design*, *12*(4), 795-819. https://doi.org/10.1080/14680629.2011.9713895

Pipintakos, G., Vincent Ching, H. Y., Soenen, H., Sjövall, P., Mühlich, U., Van Doorslaer, S., Varveri, A., Van den bergh, W., & Lu, X. (2020). Experimental investigation of the oxidative ageing mechanisms in bitumen. *Construction and Building Materials*, *260*, 119702. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2020.119702

Rowe, G., King, G., & Anderson, M. (2014). The Influence of Binder Rheology on the Cracking of Asphalt Mixes in Airport and Highway Projects. *Journal of Testing and Evaluation*, *42*(5), 1063-1072. https://doi.org/https://doi.org/10.1520/JTE20130245

Rowe, G. M., & Sharrock, M. J. (2016). Cracking of asphalt pavements and the development of specifications with rheological measurements. (Ed.),^(Eds.). 6th Eurasphalt & Eurobitume Congress, Prague, Czech Republic.

Soenen, H., Lu, X., & Redelius, P. (2008). The Morphology of Bitumen-SBS Blends by UV Microscopy. *Road Materials and Pavement Design*, *9*(1), 97-110. https://doi.org/https://doi.org/10.1080/14680629.2008.9690109

Yan, C., Huang, W., Xiao, F., Wang, L., & Li, Y. (2018). Proposing a new infrared index quantifying the aging extent of SBS-modified asphalt. *Road Materials and Pavement Design*, *19*(6), 1406-1421. https://doi.org/https://doi.org/10.1080/14680629.2017.1318082

Yan, Y., Roque, R., Cocconcelli, C., Bekoe, M., & Lopp, G. (2017). Evaluation of cracking performance for polymer-modified asphalt mixtures with high RAP content. *Road Materials and Pavement Design*, *18*(sup1), 450-470. https://doi.org/https://doi.org/10.1080/14680629.2016.1266774

Yan, Y., Roque, R., Hernando, D., & Chun, S. (2019). Cracking performance characterisation of asphalt mixtures containing reclaimed asphalt pavement with hybrid binder. *Road Materials and Pavement Design*, *20*(2), 347-366. https://doi.org/https://doi.org/10.1080/14680629.2017.1393002

Yildirim, Y. (2007). Polymer modified asphalt binders. *Construction and Building Materials*, *21*(1), 66-72. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2005.07.007

Yut, I., & Zofka, A. (2011). Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy of Oxidized Polymer-Modified Bitumens.

Applied Spectroscopy, *65*(7), 765-770. https://doi.org/https://doi.org/10.1366/10-06217

Zaumanis, M., & Mallick, R. B. (2015). Review of very high-content reclaimed asphalt use in plant-produced pavements: state of the art. *International Journal of Pavement Engineering*, *16*(1), 39-55. https://doi.org/https://doi.org/10.1080/10298436.2014.893331