Does the wet addition of crumb rubber and emission reduction agents impair the rheological performance of bitumen?

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Abstract: Crumb rubber modified bitumen (CRMB) is a promising solution for recycling waste tyres and improving asphalt performance. Nonetheless, higher temperatures are usually required during mixing, which increases the emission of volatile organic compounds (VOCs) that can potentially cause harmful health effects on workers due to their toxic and carcinogenic properties. Emission reduction agents (ERAs) have been developed to address this issue. However, limited scientific evidence is available regarding their impact on the rheological performance of CRMB, which makes the selection of the most suitable ERA challenging. This study investigated the effects of three ERAs on the physical and rheological properties of CRMB: steam-activated carbon/charcoal (AC), fly ash-based geopolymer (GFA), and Portland cement paste (PCP). In addition to penetration and softening point tests, a dynamic shear rheometer (DSR) was used to evaluate the rheological properties of the samples in the frequency and temperature domains and to perform the multiple stress creep recovery (MSCR) and linear amplitude sweep (LAS) tests. The results revealed that the three ERAs increased the stiffness of CRMB: penetration reduced and softening point, penetration index, and viscosity increased. This stiffening effect caused a drop in the fatigue resistance measured in the LAS test. Out of the three ERAs evaluated, AC clearly induced the greatest changes in binder properties. However, MSCR results, crossover frequency, R-value, Glower-Rowe parameter, and ΔTc were less sensitive to the addition of ERAs. It was concluded that the addition of GFA and PCP did not impair the physical and rheological properties of CRMB, yielding results comparable to those of a PMB. However, AC may introduce issues during mixing and service life due to the increase in viscosity and the reduction in fatigue resistance.

Keywords: volatile organic compounds; crumb rubber modified bitumen; emission reduction agents; physical and rheological parameters

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1. Introduction

Global tyre production reached 19 million tons in 2019 [1]. According to the European Tyre Rubber Manufacturers Association, 5.1 million tonnes of tyres were produced in the European Union in 2020 [2]. In addition, millions of used tyres reach the end of their service life every year and fall into the category of end-of-life tyres (ELTs) [3]. The rubber employed in the fabrication of tyres is very resilient, which leads to a great potential to be reused. Alternative final destinations for ELTs are explored since landfill disposal has been banned in most countries. Reusing and recycling are preferable options for this high-quality material as it can be used to reduce the consumption of raw materials. Due to governmental support in Europe for recycling and increasing concerns about waste growth, new end markets are being developed to find a better destination for ELTs [4]. One solution is the development of rubberised bitumen for road construction using tyre-derived crumb rubber (CR) from ELTs to address pavement performance issues and tackle the disposal problem of ELTs. CR blended into bitumen is considered to improve asphalt pavement performance in terms of high-temperature stability, fatigue life and cracking resistance, and a solution for waste tyre recycling technology [5-7].

Nonetheless, incorporating CR into bituminous mixtures raises certain issues, such as limited pumpability, mixability, and workability, as well as the need for additional energy to heat the materials during the mixing and compaction processes [8]. The interaction between CR and bitumen is a physical interaction, characterized by the absorption of the aromatic fraction (maltenes) of the binder by the CR through diffusion. This occurs as the maltenes of the bitumen and CR exhibit similar solubility parameters, which leads to

enhanced compatibility between them [9]. The absorption of maltenes combined with a decrease in the oily fraction of the binder causes the CR particles to swell, which increases the viscosity of crumb rubber modified bitumen (CRMB) [10].

To overcome the increase in viscosity, asphalt mixtures using CRMB require a higher temperature than those with a traditional binder. This leads to an increase in the emission of fumes, odour, and volatile organic compounds (VOCs) like toluene, ethylbenzene, xylenes, and sulphur compounds [11-15], which poses a risk to pavement construction workers and also affects the growth and development of animals and plants [16-19]. Higher temperatures stimulate molecular movement and release lighter compounds [20, 21]. To reduce fume emissions, warm mix additives and emission reduction agents (ERAs) have gained attention in recent years. Warm mix technology (either with additives or using foamed bitumen) aims to reduce the viscosity of the binder and allows for a lower mixing temperature compared to hot mix asphalt. Turbay et al. [22] conducted a rheological analysis to evaluate the behaviour of CRMB when modified with warm mix additives, specifically Evotherm M1 and Iterlow T, at a dosage of 0.3% by weight of bitumen. They concluded that the use of these additives tend to slightly decrease the viscosity, stiffness and performance at high temperature of CRMB. Worse high temperature performance was also reported by Yu et al. [23] when creating foamed CRMB with different water contents. Although warm mixtures have been found to reduce the emission of VOCs, polycyclic aromatic hydrocarbons, and total suspended particles, this may come at the expense of the final performance [24]. For that reason, the addition of ERAs could be a solution to effectively reduce emissions with limited effect on performance. Despite the importance of effectively reducing VOCs, there have been limited studies about the impact of ERAs on the rheology of the binder. Cui et al. [25] used 4 wt% styrene butadiene styrene (SBS) and 4 wt% active carbon filler as ERA, and

concluded that the combination of both materials significantly lowered the VOC emission and improved the deformation resistance at higher temperatures. Wu et al. [26] used mesoporous hollow silica as ERA and observed an increase in complex modulus and a decrease in phase angle and rutting factors while reducing the VOC emission. The scarcity of such studies has prompted us to explore this area thoroughly and provide valuable scientific evidence to aid in selecting the most suitable ERA for effectively reducing VOC emissions while maintaining optimal binder performance.

2. Objectives and scope

The objective of this study is to investigate the impact of ERAs on the physical and rheological properties of CRMB. In addition, a comparative analysis with commercially available unmodified (base) and polymer-modified bitumen (PMB) was conducted to offer insights into the advantages and potential drawbacks of utilizing CR and different ERAs for improving binder performance while reducing VOC emissions.

Steam-activated carbon/charcoal (AC), fly ash-based geopolymer (GFA), and Portland cement paste (PCP) were selected as ERAs based on their potential to reduce VOC emissions from CRMB evaluated in a prior study [15]. Table 1 shows the summary of the results obtained in the prior study for total VOC emission (TVOC) rate considering all measured VOCs, most significant VOCs released when CR was added to the binder, and VOCs classified as health hazards, acute toxic or environmental hazards according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [27].

Table 1. VOC emission rate for CR modified bitumen blends (in μmol/m^2) [15]

	TVOC*	**Hazardous VOCs****	**CR VOCs*****
Base	60.0	42.0	25.4
PMB	114.9	92.6	63.8
CRMB	108.2	78.8	65.7
CRMB+AC	55.4	34.2	26.9

	TVOC*	Hazardous VOCs**	CR VOCs***
CRMB+GFA	56.5	34.8	21.7
CRMB+PCP	45.3	30.0	21.0

* TVOC: total VOC emission rate considering all VOCs measured

** Hazardous VOCs: classified as health hazards, acute toxic or environmental hazards according to the GHS

***CR VOC: most significant VOCs released when CR was added to a base bitumen

Note: all samples were heated up to 180 °C over 320s

3. Materials and Methods

This study comprised a combination of empirical and rheological tests to evaluate the impact of ERAs on the performance of CRMB. The experimental methods are illustrated in Figure 1 and described in detail in the following subsections. The physical characteristics were determined by means of standard penetration and softening point tests. A dynamic shear rheometer (DSR) was used to evaluate the rheological properties of the samples in the frequency and temperature domains and to perform the multiple stress creep recovery (MSCR) and linear amplitude sweep (LAS) tests. Comparisons were also made with unmodified virgin bitumen and a commercially available polymer-modified bitumen (PMB).

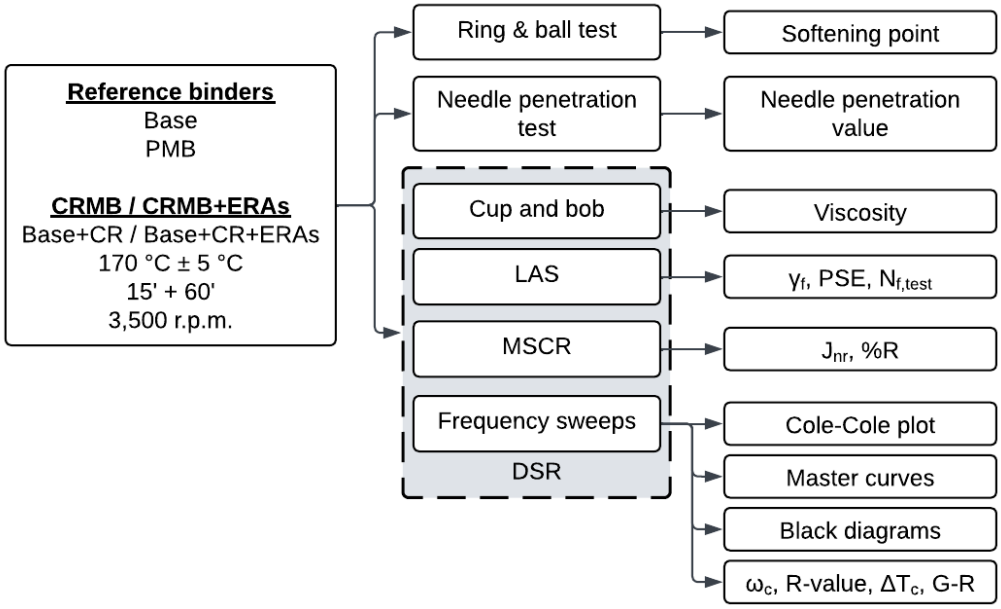

Figure 1. Flowchart of the experimental method

3.1. VOC emission reduction agents

Steam-activated carbon/charcoal was supplied by Alfa Aesar. Ordinary Portland cement (OPC) was provided by Sibelco and was activated using distilled water to create a Portland cement paste (PCP). Fly ash (FA) class F, supplied by Value Ash Technologies, was used as precursor material to synthesise the geopolymer-based additive. The alkaline activator was composed of sodium hydroxide (98% pure, pellets) and a sodium silicate solution (initial composition of 25.9 wt.% of sodium oxide, 7.9 wt.% of silicon oxide, and 66.2% water). Table 2 shows the formulation of the FA-based geopolymer (GFA) paste and PCP paste. PCP and GFA were then sealed and placed in an oven at 60 °C for 3 days. Before being used, AC, GFA, and PCP were milled and the fraction passing the 0.125 mm sieve was selected.

Table 2. Paste formulation

	FA (g)	**OPC (g)**	**NaOH (g)**	**Na_2SiO_3 (g)**	**Water (g)**
GFA	45.00	-	1.38	9.43	11.45
PCP	-	45.00	-	-	18.00

A Mastersizer Hydro 2000G Particle Size Analyser (Malvern, UK) was used to measure the differential and cumulative volumes for each ERA and these results are shown in Figure 2. To disperse the agglomerates, the powders were subjected to ultrasonic agitation. The results showed that GFA had the smallest mean particle size (6.71 µm), followed by AC (24.87 µm) and PCP (28.71 µm).

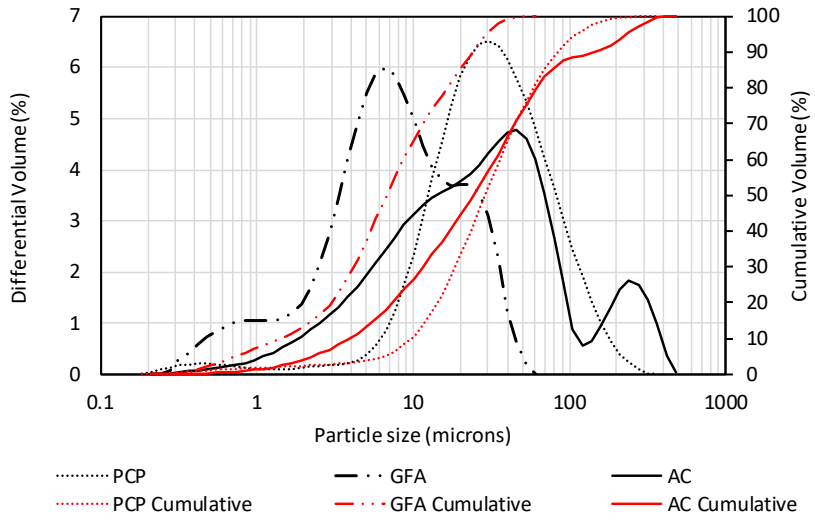

Figure 2. Differential (in black) and cumulative (in red) volumes of the emission reduction agents.

3.2 Bitumen

A unmodified bitumen (base) with a pen grade of 50/70 was used as the base binder for crumb rubber modification, and a polymer modified bitumen (PMB) with a grade of 10/40-65 was used for comparison purposes. Both binders are readily available in the Belgian market, with the PMB being formulated through the crosslinking of bitumen and a thermoplastic elastomer. The penetration values, softening points, and penetration indices of both binders are reported in Table 3.

Table 3. Mechanical properties of the reference binders

Property	Test Standard	Results		Unit
		Base	PMB	
Penetration (at 25 °C)	EN 1426	53.0	21.0	0.1 mm
Softening point	EN 1427	51.8	69.0	°C
Penetration index	-	- 0.6	0.7	-

3.3 Crumb rubber

The base bitumen was modified with a crumb rubber source produced by ambient grinding. This process leads to irregularly shaped particles with relatively high surface

area, which improves the interaction between CR and binder [5]. Figure 3 displays that the CR fraction used for bitumen modification passed the 0.5 mm sieve.

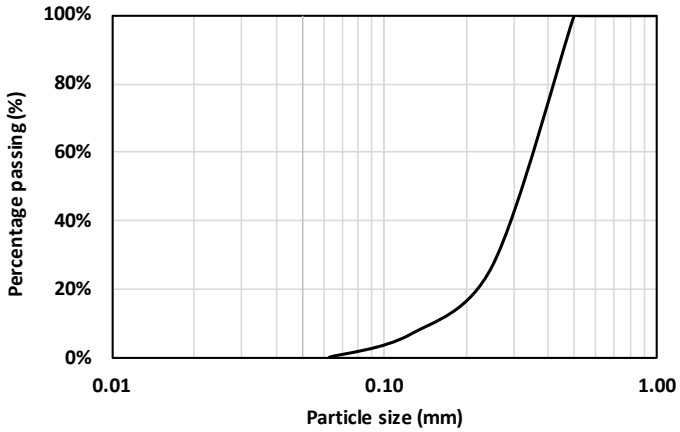

Figure 3. Gradation curve of the fraction of the CR used to modify the base binder

A Q50000IR Thermogravimetric Analyzer (TA Instruments) was used to determine the following composition of CR by weight: 9.14% oils and volatiles, 53.73% natural and synthetic rubber, 28.51% carbon black, and 8.62% inert filler.

3.4 Blending process

The crumb rubber modified bitumen (CRMB) was prepared by blending the base bitumen (500 g) at 170 °C ± 5 °C with the CR particles. Previous studies consistently reported that the typical rubber content in CRMB ranges between 10% to 20% by weight of the bitumen [28-30]. The decision to include 15% of CR by mass of bitumen was informed by prior findings [31], which demonstrated that this proportion resulted in reduced temperature susceptibility and enhanced binder elasticity. To ensure proper digestion of the CR into the bituminous matrix, a high shear mixer with a speed of 3,500 r.p.m. was employed for 75 min (15 min to reach temperature equilibrium followed by 60 min at 170 °C ± 5 °C). A heating mantle was utilised to keep the temperature at 175 °C. For blends with ERAs, the ERA was incorporated into the bitumen prior to the

addition of CR, with a mass ratio of 5.75% relative to the bitumen. The ERA ratio of 5.75% by weight of bitumen was explored in previous studies [15, 32, 33]. The samples were labelled as presented in Table 4.

Table 4. Summary of the bituminous blends and their composition (% by mass of bitumen)

Name	CR content	ERA content	ERA type
CRMB	15.0	-	-
CRMB+AC	15.0	5.75	Steam-activated carbon/charcoal
CRMB+GFA	15.0	5.75	Ground granulated blast furnace slag-based geopolymer
CRMB+PCP	15.0	5.75	Portland cement paste

3.5. Experimental methods

3.5.1 Empirical binder tests

Softening point and needle penetration values were determined according to EN 1427:2015 and EN 1426:2015, respectively. In order to obtain a quantitative measurement of temperature susceptibility, the penetration index (PI) was calculated based on the softening point (SP) and penetration values at 25 °C (PEN) following Eq. (1) [34].

$$\mathrm{PI} = \frac{1952 - 500\log(PEN) - 20\,SP}{50\,\log(PEN) - SP - 120} \quad (1)$$

3.5.2 Rheological tests

Viscosity – High temperature

The viscosity of bitumen at high temperatures is considered a vital property as it represents the binder's mixability, pumpability, and workability. A bob and cup feature was used in the DSR to measure the viscosity in accordance with EN 13302 in a

temperature range from 135 to 177.5 °C. Unmodified binders generally behave like a Newtonian fluid, where their viscosities are independent of the shear rates. On the other hand, modified binders normally show a non-Newtonian behaviour that is dependent on shear rate and temperature, with viscosities decreasing as the shear rate increases [35]. For that reason, a prolonged period was adopted before taking the readings in a range of shear rates from 1 to 100 s^{-1} at 5 s^{-1} intervals. For comparison purposes, the specific shear rate highlighted in this study corresponds to 100 s^{-1} for all temperatures, representing the region where the blends demonstrate a Newtonian behaviour.

The viscous behaviour of the binder can be attributed to a thermally activated process, where molecules must overcome energy barriers to move within the material. The intermolecular forces during the flow of asphalt create resistance, and this resistance is governed by the activation energy, which represents the minimum energy required to overcome it. The determination of this energy can help understand if the incorporation of crumb rubber as a modifier changes the thermally activated resistance of the base binder [36]. The Arrhenius model, Equation (2), was used to determine the activation energy, where η is the viscosity of the bituminous binder, T is the temperature in degree Kelvin, A is a model constant, R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), and E_f is the activation energy. A more concise representation of Equation (2) is shown in Equation (3), where the slope of ln (η) versus 1/T is equal to E_f/R, given the linear trend observed.

$$\eta = Ae^{\frac{E_f}{KT}} \tag{2}$$

$$\ln \eta = \frac{E_f}{RT} + \ln A \tag{3}$$

Frequency sweeps

To evaluate the effect of the ERAs on the rheological properties of CRMB, frequency sweeps were conducted on unaged samples using a dynamic shear rheometer (DSR) from Anton Paar. For the high frequency-low temperature range (-30 °C to +10 °C), a 4 mm parallel plate geometry with a 1.75 mm gap was utilised. For the higher temperature ranges of 0 to +40 °C and +30 to +70 °C, parallel plates were utilised with gaps of 2 and 1 mm, and diameters of 8 and 25 mm, respectively. Frequency sweeps ranging from 0.1 to 10 Hz were conducted under strain control. Optimal strain levels of 0.05% and 1% were used for performing strain-controlled frequency sweeps within the linear viscoelastic region for the 8 mm and 25 mm plates, respectively. The storage (G') and loss moduli (G") measured by the DSR were utilised to calculate the complex shear modulus (G*) and phase angle (δ).

Master curves were built by processing the raw data with the rheological software RHEA ^{TM} (by Abatech Engineering Consultants [37]). The Christensen-Anderson (CA) mathematical model was used to build the master curves at a reference temperature of 15 °C [38, 39]. The CA model, Equation (4), defines the complex shear modulus (G*) as a function of frequency based on the glassy modulus (G_g), the rheological shape parameter (R), and the crossover frequency (ω_c), which is the frequency at which G' and G" are equal. The difference between the log of G_g and the crossover modulus (G_c), where G'=G''=G_c, is expressed by the shape parameter R. While the R parameter expresses the variation in relaxation properties, ω_c indicates the transition point between an elastic and a more viscous behaviour [40]. A graphical representation of the parameters defined in the CA model is shown in Figure 4.

$$G^*(\omega) = G_g * \left[1 + \frac{\omega_c}{\omega}^{(log2/R)}\right]^{-R/log2} \quad (4)$$

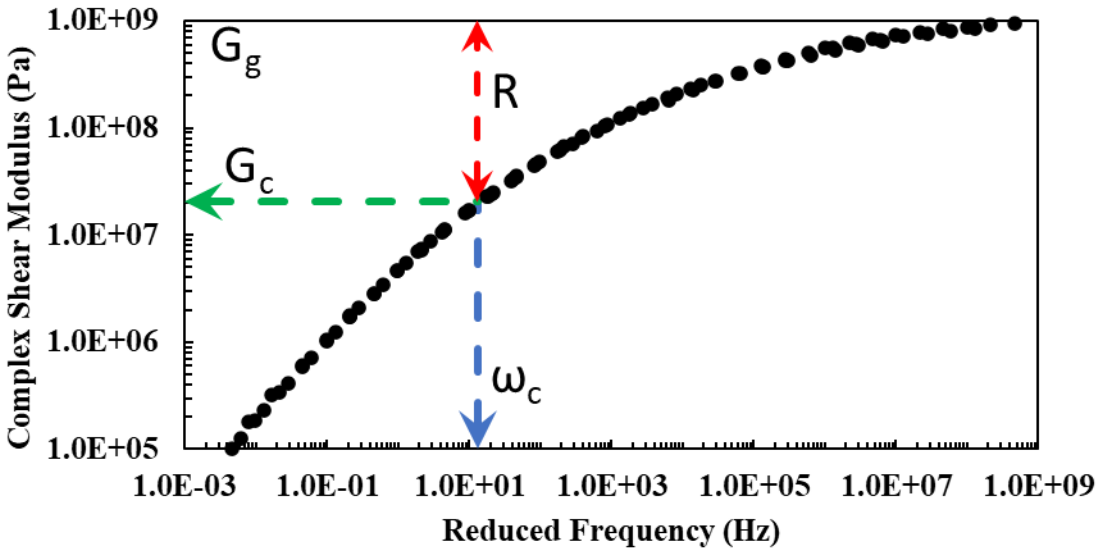

Figure 4. Graphical representation of the glassy modulus (G_g) the rheological shape parameter (R), and the crossover frequency (ω_c).

The Black diagram is a representation of the raw rheological data and is commonly used to evaluate the impact of polymer modification on the rheological characteristics of a modified bitumen. This diagram is generated by collecting the phase angle and complex shear modulus under various temperature and frequency conditions. When examining the diagram, a smooth curve indicates a binder that exhibits the expected response of time-temperature equivalence, which is typically observed in unmodified binders. Conversely, discontinuities within the diagram suggest the presence of bitumen with high wax content, highly polymer modified bitumen, or a binder with a highly asphaltene structured composition [41].

The Glover-Rowe (G-R) parameter is associated with fatigue cracking [42]. It is calculated according to Equation (5) using the G* and δ measured at a test temperature of 15 °C and a frequency of 0.005 rad/s [43]. In this study, the G-R parameter was estimated from the RHEA ^{TM} software based on the full CA master curves. Two damage thresholds have been proposed for the G-R parameter: G-R = 180 kPa suggests onset

cracking (warning) and G-R = 600 kPa indicates significant cracking (critical) [44]. Higher values of G-R indicate more brittle asphalt binders that are more susceptible to fatigue cracking, as it has been demonstrated in other studies [45-47]. The G-R thresholds should be understood as an indication of possible crack formation, rather than being regarded as an absolute classification criterion, considering the specific circumstances for which they were identified.

$$\text{G-R} = \frac{G^* * (\cos\delta)^2}{\sin\delta} \quad (5)$$

ΔT_c – Low temperature

As the frequency sweep measurements covered the low-temperature range (up to -30 °C), an extra analysis was conducted to evaluate blend behaviour at lower temperatures. Instead of relying on the conventional bending beam rheometer (BBR) method, the relaxation parameter m-value and creep stiffness S(t) were derived from low-temperature DSR data [48, 49]. These parameters play a crucial role in determining ΔT_c, a proposed indicator of both ageing-induced cracking and the evolution of ageing processes [47]. In a BBR test, the two lower continuous grading temperatures, $T_{c,S}$, and $T_{c,m}$, are determined by a stiffness G of 300 MPa and a slope (m) of 0.3 at 60 s, respectively. However, the following conversions proposed by Christensen et al. [48] need to be applied when estimating ΔT_c from DSR tests: G = 143 MPa and m = 0.275 at 60 s. As per the aforementioned studies, this conversion yields a satisfactory correlation between BBR and DSR measurements. The determination of the continuous grading temperatures, $T_{c,G}$, and $T_{c,m}$, was carried out by applying Equations (6) and (7), respectively, in accordance with the procedures specified in ASTM D7643-16. As outlined in the standard, the temperature difference between these values, denoted as ΔT_c — Equation (8). Two

relaxation moduli (G_1 and G_2) and two relaxation slopes (m_1 and m_2) at two temperatures (T_1 and T_2) must be determined, where $G_1 \leq 143$ MPa $\leq G_2$ and $m_1 \leq 0.275 \leq m_2$. Binders with lower (i.e., more negative) ΔT_c values are more susceptible to thermal cracking, as they exhibit lower stress relaxation properties. Two limits have been proposed for ΔT_c as performance indicators: -2.5 °C and -5 °C as warning and critical limits, respectively [47]. In accordance with ASTM D7643-16, the samples were short- and long-term aged using the rolling thin film oven (RTFO, EN 12607-1) test at a temperature of 163 °C for 75 min, followed by the pressure ageing vessel (PAV, EN14769) test, at a temperature of 100 °C and air pressure of 2.1 MPa for 20 h.

$$T_{c,G} = T_1 + \frac{(T_1 - T_2) * (\log 143 + \log G_1)}{\log G_1 - \log G_2} - 10 \quad (6)$$

$$T_{c,m} = T_1 + \frac{(T_1 - T_2) * (0.275 + m_1)}{m_1 - m_2} - 10 \quad (7)$$

$$\Delta T_c = T_{c,G} - T_{c,m} \quad (8)$$

Linear amplitude sweep (LAS) – Intermediate temperature

In order to evaluate the fatigue resistance of the blends, the LAS test was performed. It has been proposed as an alternative to the fatigue parameter $G^* \cdot \sin \delta$ introduced by SHRP, as this was later found to have a poor correlation with the fatigue performance of asphalt mixtures [50]. Conversely, the bitumen fatigue life estimated from the LAS test has shown a reliable correlation with the fatigue resistance of asphalt mixtures [51, 52]. As described in AASHTO TP 101, the LAS test is performed on a DSR equipped with an 8 mm parallel plate geometry at a constant temperature (15 °C for this study) on samples

after RTFO+PAV. The first stage of the LAS test is a frequency sweep from 0.2 to 30 Hz to define the undamaged properties and the damage evolution parameter at a strain level of 0.1 % (to ensure the binder strain is within the linear viscoelastic region). The second stage is the linear amplitude strain sweep from 1 % to 30 % over 3000 cycles at 10 Hz. The failure criterion used in the LAS test was the peak in stored pseudo strain energy (PSE), which indicates a loss in the material's capacity to store additional PSE as strain increases [53]. The number of cycles corresponding to the peak in stored PSE ($N_{f,test}$) was selected as the binder performance parameter in the LAS test [54].

Rutting Resistance Indicator (MSCR test) – High temperature

The MSCR test was introduced as a promising method to examine the elasticity and stress dependence of modified binders. The MSCR test was performed in accordance with EN 16659 at 50 °C. The temperature selection for this test was based on its correspondence to the rutting test temperature specific to the Flemish region in Belgium. The entire series of binders were short-term aged using the RTFO test. A 25 mm parallel plate geometry with a 1 mm gap setting was used and the samples were loaded at a constant stress for 1 s followed by 9 s of recovery. The stress levels of 0.1 kPa and 3.2 kPa were applied on each sample over ten cycles, and two main parameters were calculated: the non-recoverable creep compliance (J_{nr}) and recovery percent (R%). J_{nr} is the ratio between the residual strain and the stress applied and has been proposed as an alternative for the traditional rutting parameter ($G^*/\sin \delta$). R% represents the amount of strain recovered by the binder after repeated loading and unloading.

4. Results and discussion

Table 5 presents a comprehensive summary of all binder test results. This table will be instrumental in facilitating the subsequent discussion of the results.

277 Table 5. Physical and rheological properties of all blends

Tests	Parameters	Condition	Units	Base	PMB	CRMB	CRMB+AC	CRMB+GFA	CRMB+PCP
Empirical	Penetration at 25 °C	Unaged	0.1 mm	53.0	21.0	34.0	27.0	30.0	30.0
	Softening point	Unaged	°C	51.8 ± 0.1	69.0 ± 0.1	64.6 ± 0.1	68.8 ± 0.2	65.2 ± 0.2	65.4 ± 0.2
	Penetration index	Unaged	-	-0.6	0.7	1.0	1.2	0.8	0.8
Viscosity	Dynamic viscosity at 135.0°C	Unaged	Pa·s	0.68 ± 0.01	3.21 ± 0.01	2.62 ± 0.02	4.09 ± 0.01	2.84 ± 0.03	2.84 ± 0.01
	Dynamic viscosity at 177.5°C	Unaged	Pa·s	0.11 ± 0.01	0.37 ± 0.01	0.44 ± 0.01	0.65 ± 0.01	0.46 ± 0.01	0.46 ± 0.01
	Activation energy (E_f)	Unaged	kJ/mol	67.83	74.70	70.05	71.71	71.08	71.03
Frequency sweeps	Crossover frequency (ω_c)	Unaged	Hz	12.87 ± 0.38	0.28 ± 0.01	0.21 ± 0.01	0.13 ± 0.01	0.22 ± 0.01	0.2 ± 0.02
	R-Value	Unaged	-	1.75 ± 0.01	2.23 ± 0.01	2.68 ± 0.02	2.73 ± 0.01	2.67 ± 0.01	2.70 ± 0.01
	G-R	Unaged	kPa	2.60 ± 0.3	53.35 ± 2.53	40.53 ± 0.41	67.68 ± 3.33	45.84 ± 1.16	48.19 ± 3.62
	$T_{c,G}$	RTFO+PAV	°C	-16.59 ± 0.67	-12.04 ± 0.35	-23.27 ± 0.74	-22.23 ± 0.25	-21.03 ± 0.38	-22.53 ± 0.08
	$T_{c,m}$	RTFO+PAV	°C	-13.70 ± 0.24	-7.66 ± 0.10	-14.47 ± 0.43	-13.85 ± 0.47	-13.60 ± 0.10	-13.75 ± 0.17
	ΔT_c	RTFO+PAV	°C	-2.89 ± 0.42	-4.38 ± 0.25	-8.80 ± 0.31	-8.38 ± 0.22	-7.43 ± 0.38	-8.77 ± 0.09
LAS	γ_f	RTFO+PAV	%	14.70	14.40	19.40	13.50	17.10	15.50
	Maximum stored PSE	RTFO+PAV	-	3.37	6.62	1.76	1.73	1.69	1.66
	$N_{f,test}$	RTFO+PAV	Cycles	1400	1370	1890	1280	1650	1490
MSCR	$J_{nr\ 0.1}$	RTFO	1/kPa	2.30	0.56	0.59	0.53	0.62	0.52
	$J_{nr\ 3.2}$	RTFO	1/kPa	2.34	0.55	0.62	0.54	0.64	0.51
	$R_{0.1}$	RTFO	%	53.71	76.26	83.56	83.81	83.09	83.29
	$R_{3.2}$	RTFO	%	52.62	76.88	82.84	83.44	82.48	83.32

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4.1. Empirical binder tests

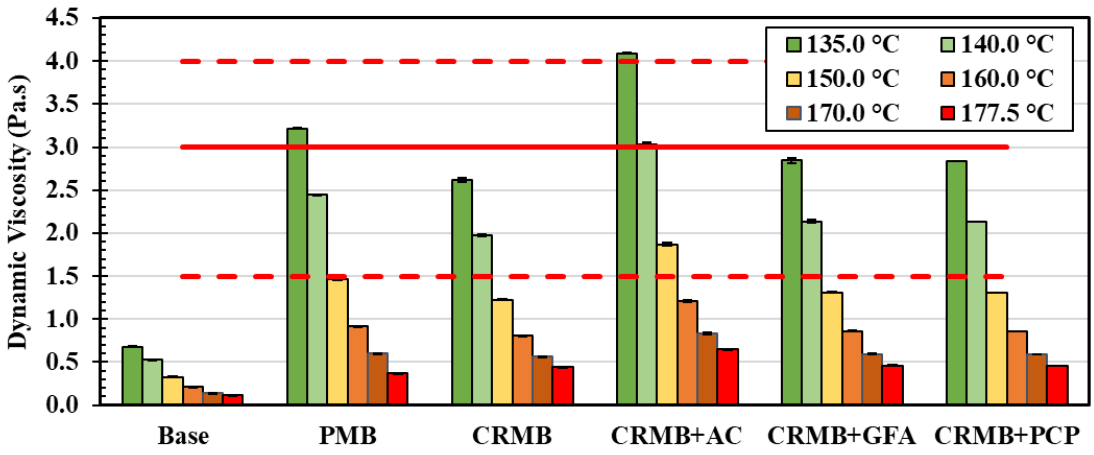
The results of the penetration and softening point tests are shown in Table 5. The incorporation of CR reduced the penetration value (the binder became stiffer) and increased the softening point to a level closer to that of PMB. The effect of polymer modification can be observed by the positive PI. The addition of ERAs led to a reduction in penetration levels and an increase in the softening point compared to CRMB. This trend aligns with the findings from Tang et al. [55], who observed a similar effect when adding geopolymer additives (6% by weight of bitumen) to an unmodified binder. The incorporation of AC to the blend resulted in a higher PI due to a lower penetration value and a higher SP. GFA and PCP showed similar results between each other and closer to those of CRMB.

4.2. Rheological tests

Viscosity

Figure 5 shows the dynamic viscosity of the samples measured at different temperatures. The base binder behaved like a Newtonian fluid, whose viscosity is independent of the shear rate, but changed with temperature (0.68 Pa·s at 135 °C and 0.11 Pa·s at 177.5 °C). The PMB had a behaviour similar to a Newtonian fluid as little to no difference was observed for the different temperatures applied, showing values from 3.21 Pa·s at 135 °C to 0.37 Pa·s at 177.5 °C. Of note, the PMB exceeded the value of 3 Pa·s at 135 °C prescribed by the Superpave™ specification. For a wide temperature range (from 135 up to 177.5 °C) CRMB, CRMB+GFA and CRMB+PCP showed similar viscosity values. Conversely, CRMB+AC exhibited a 45% higher viscosity on average for the same temperatures compared to the other CR modified blends. This is consistent with the stiffer

response observed in the penetration test. If a maximum viscosity of 3 Pa·s at 135 °C is to be met, all blends modified with CR would pass this requirement, with the exception of CRMB+AC. This would have to be heated to a temperature between 140 and 150 °C to reach a viscosity of 3 Pa·s. As reported by Jamal et al. [56], the recommended worldwide viscosity for CR specifications should be below a threshold that varies between 1.5 and 4.0 Pa·s at 177.5 °C. In this case, all blends would easily pass this requirement.

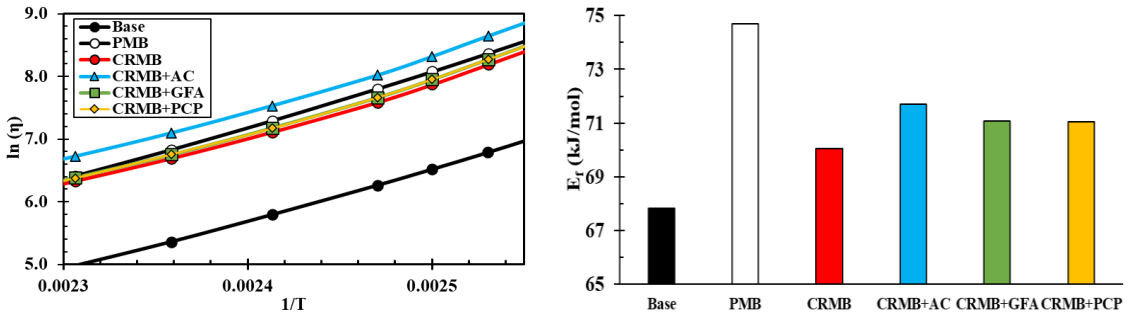


Note: Continuous red line: limit at 135 °C proposed by the Superpave™ specification. Dashed red line: different limits for CRMB found in literature.

Figure 5. Viscosity measured with the cup and bob setup in the DSR for all samples at different temperatures

Figure 6 plots ln (η) versus 1/T and the activation energy as determined by the slope of their relationship. The results indicate that the incorporation of crumb rubber as a modifier increased the activation energy, which results in an increased resistance to flow of the binder. The addition of CR leads to the migration of bitumen oils into the CR particles through diffusion causing swelling of CR particles, reducing inter-particle distance, thus also increasing the viscosity of the bituminous component [57]. The addition of ERAs to CRMB further increased the activation energy of the binder. Furthermore, it is worth

noting that among the three ERAs, AC increased the activation energy more than GFA and PCP. This indicates that incorporating AC as an ERA leads to an increase in the energy required to overcome the fluid resistance forces between the hydrocarbon chains, which aligns with the findings from dynamic viscosity measurements.



(a) (b)

Figure 6. (a) Ln of viscosity (η) versus the inverse of temperature (1/T) and (b) the activation energy (E_f) for all binders

Frequency sweeps

A Cole-Cole plot provides a graphical representation of the stiffness of a material and depicts the contribution of the material elastic (storage modulus – G') and viscous (loss modulus – G") components to its overall stiffness. The point at which G' equals the G" is known as the crossover frequency (ω_c), and its inverse is referred to as the relaxation time. Consequently, a line at a 45° angle indicates the position of the G' = G" points. Any points above this line exhibit a viscous-dominant phase, while points below the line display an elastic-dominant phase. The Cole-Cole plot for all blends is shown in Figure 7. In the case of the base binder, the lower stiffness range exhibited a significant proportion of the material response being governed by its viscous component. This indicates that the material behaves more like a liquid and loses its capacity to retain applied energy. Consequently, a substantial amount of this energy is dissipated, leading to a higher value

of G". By incorporating CR into the base binder, both the overall stiffness and the ratio of the elastic to the viscous components were increased, showing values similar to PMB, particularly at lower stiffness values. The migration of bitumen oils into the CR particles through diffusion, as previously mentioned, caused the binders modified with CR to become stiffer. It can be seen that the addition of all ERAs had a minimal effect on the relative contribution of the viscous and elastic components over the entire range of stiffness values.

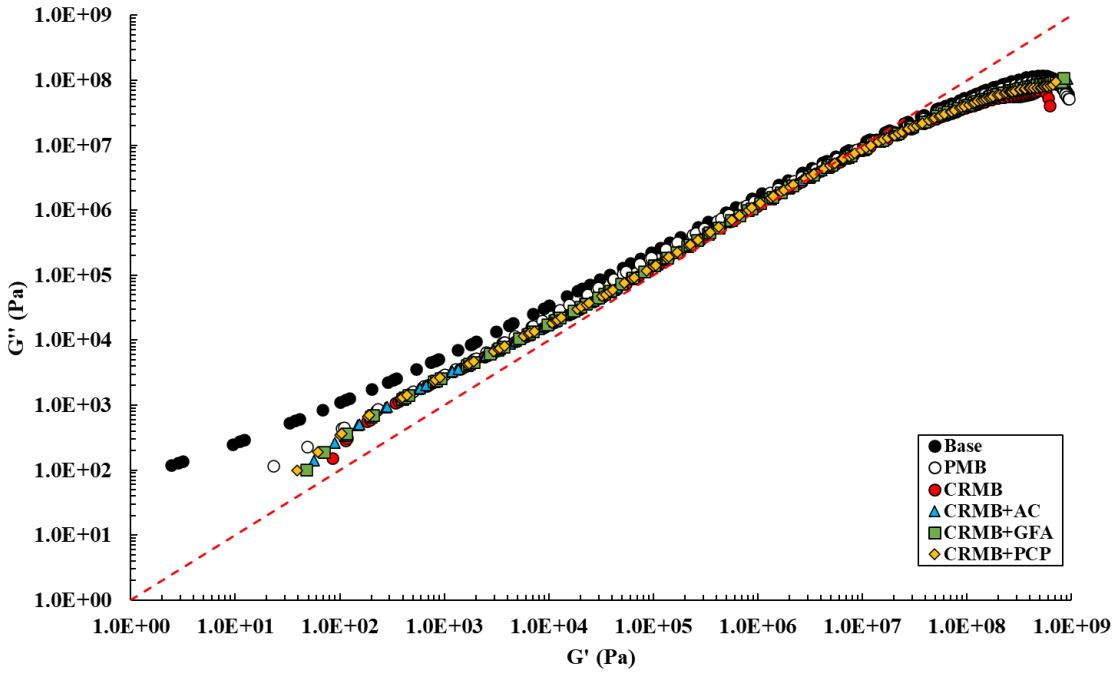
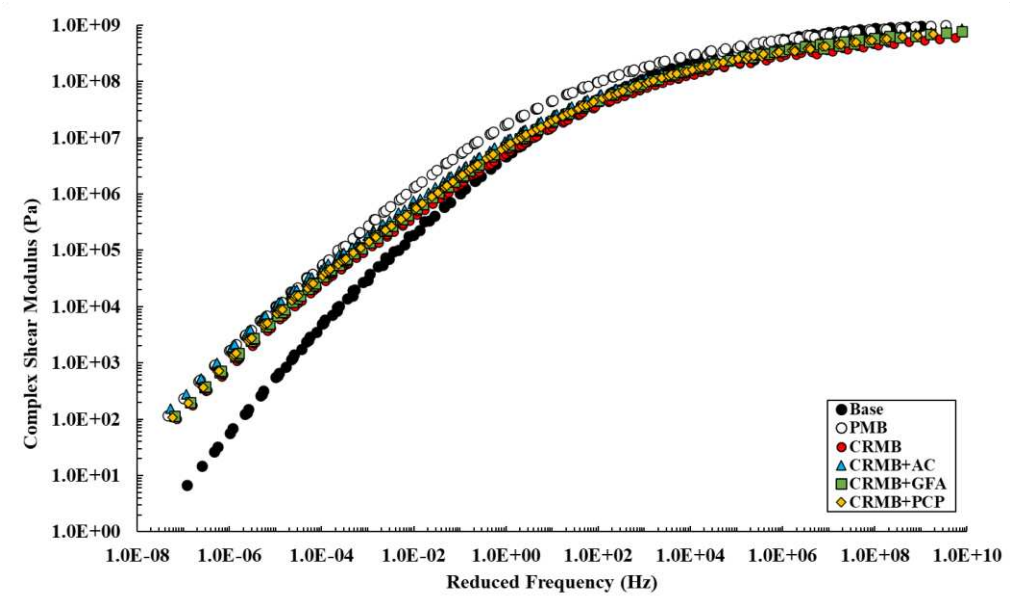


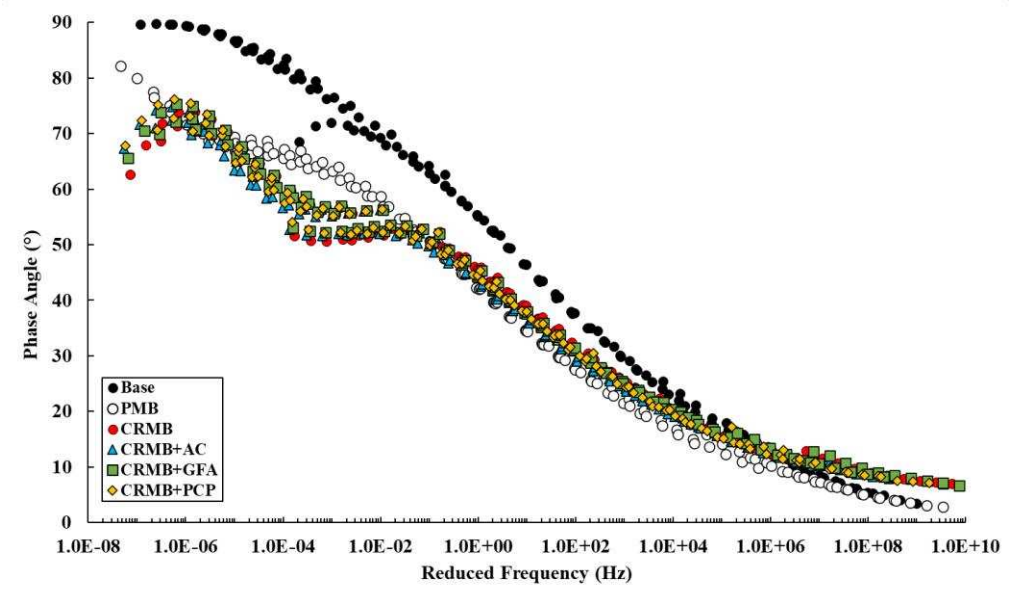
Figure 7. Cole-Cole plot for all blends

The complex shear modulus master curves of the samples are presented in Figure 8a. The introduction of CR increased the stiffness of the binder in the lower frequency-high temperature domain. This is advantageous from a performance standpoint as it improves the resistance to rutting. Conversely, the complex shear modulus of CRMB was lower than that of the base binder for the higher frequencies (low temperature domain). The same behaviour was observed for the CRMB samples modified with ERAs, but with a vertical shift in the G* master curve, which can be translated as an increase in stiffness

for all temperatures/frequencies compared to CRMB. A flatter curve can also be seen for the CR modified blends, indicating a more gradual transition from a solid to a fluid state, as it represents the disparity between the glassy modulus and the modulus at the crossover frequency. Among all CR blends, CRMB+AC exhibited slightly higher complex shear moduli throughout the range of frequencies, which substantiates that the incorporation of AC contributed to increased stiffness and resistance to deformation.



(a)



(b)

Figure 8. Influence of the use of ERAs and CR on the complex shear modulus (a) and phase angle (b) master curves

Figure 8b shows the phase angle master curves of all samples. The addition of CR reduced the phase angle throughout almost the entire range of frequencies, being rather remarkable at the lower frequencies (high-temperature domain). The lower phase angle at high temperatures indicates a more elastic response of the binder; hence the material can better recover its shape and resist deformation under dynamic loading conditions, which helps to reduce permanent deformation. A plateau is evident between the reduced frequencies of 1.0E-04 Hz and 1.0E-01 Hz for all CR modified binders. Notably, this plateau displays varying phase angle values at the same reduced frequencies. This demonstrates the dual-phase nature of the binder and the influence of the polymeric modification resulting from the presence of CR [41, 58]. The several phase angle values serve as a delineation between the bitumen-dominant phase and the polymer-dominant phase. To the right of this plateau, bitumen primarily governs the rheological behaviour and the blend characteristics resemble those of unmodified bitumen. However, at lower frequencies (high temperature domain), the base bitumen begins to soften, which makes the CR particles carry the shear load. The addition of the ERAs resulted in a slight lower phase angle at low to intermediate temperatures compared to CRMB. These results are in accordance with the findings reported by Cui et al. [25] and Wu et al. [26], who also found an increase in the complex shear modulus and a decrease in phase angle with the addition of CR and ERAs.

The CA-model yields additional parameters, namely ω_c and R-value. Table 5 revealed a reduction in the crossover frequency and an increase in R-value of all the samples following the addition of CR. This decrease in ω_c indicates that the binders modified with CR will require more time to relax stresses, specially for CRMB+AC, which may result

in the accumulation of residual stresses if the binder cannot rapidly dissipate applied stresses. On the other hand, the elevation in R-value (similar values between CRMB and samples with ERAs) signifies a flatter complex shear modulus master curve (as seen in Figure 8a), which indicates a lower temperature dependency. Other studies have also demonstrated that the R-value tends to rise with both polymer modification and binder oxidation [59].

The Black diagrams shown in Figure 9 illustrate the rheological characteristics of the CRMB blends, along with comparisons to the base and PMB binders. The curves for PMB and the blends with CR exhibit distinct differences from that of the unmodified bitumen. The curve of the base bitumen appears smoother than the trends displayed by the modified bitumen, which agrees with the expectation that unmodified bitumen is thermo-rheologically simpler [60].

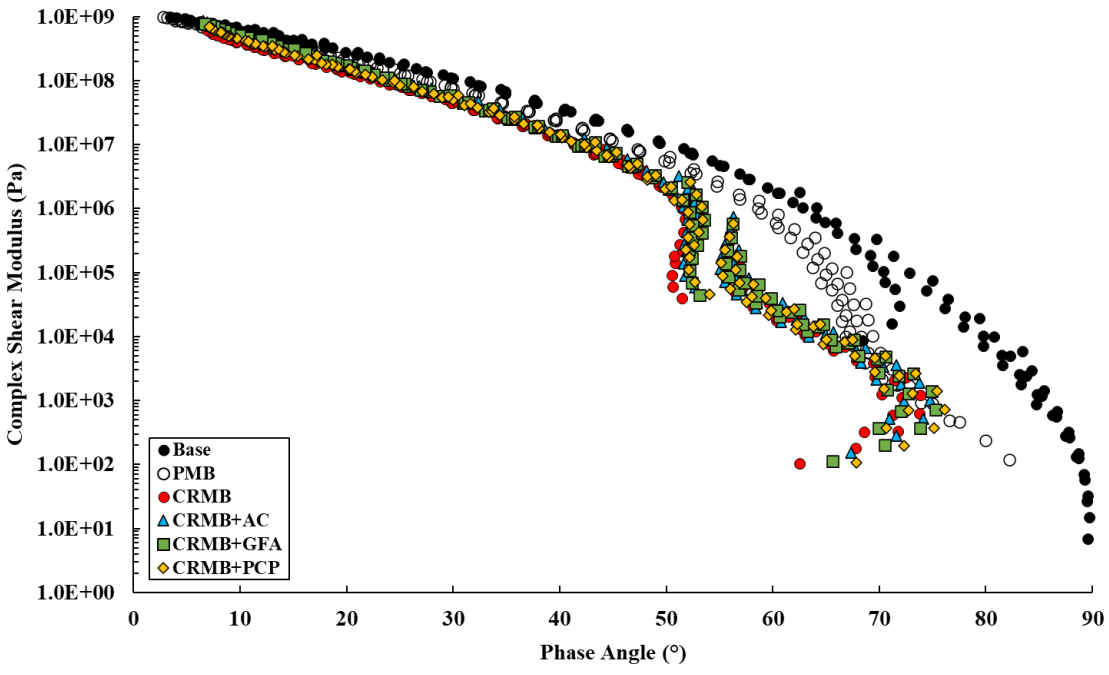


Figure 9. Influence of the addition of CR and ERAs on the Black diagram.

In the upper part of the Black diagram, where G* is greater than 10 MPa, which represents the low-temperature domain, the behaviour of the base bitumen and modified bitumen is

relatively similar. When comparing CRMB with the blends modified with ERAs, the addition of AC, PCP, and GFA did not significantly alter the rheological behaviour of CRMB besides the differences already mentioned for G* and δ. For G* below 10 MPa (temperatures above 10 °C), the PMB and the CRMB blends yielded lower phase angles than the base binder, which substantiated a more elastic response. According to Airey [61], the influence of a polymer on bitumen is primarily significant at temperatures above 10 °C. At these temperatures, the viscosity of the base bitumen decreases, which allows the elastic network of the polymer to primarily determine the mechanical properties of the blend. In addition, Airey et al. [62] demonstrated how the dominance of a polymer network of elastomeric SBS-modified bitumen exhibits a distinguishable elastic response at high testing temperatures. However, for CRMB and CRMB modified with ERAs, a rapid discontinuation after reaching a phase angle of approximately 50° was observed. This behaviour was also reported by Jamal et al. [57] and can be explained by the fact that when CR particles are added to bitumen, some are digested by the bituminous matrix while others remain insoluble. At low temperatures, the system consisting of undigested CR particles and bitumen with soluble CR particles acts as a single unit, resulting in lower overall stiffness than the base binder. As the temperature increases, the base binder undergoes a transition from a glassy state to a viscous solid and eventually to a viscous fluid. However, for CRMB, the bituminous phase softens and no longer acts as a single unit. The insoluble CR particles remain suspended without forming a long-range network due to the high viscosity of the surrounding phase around the CR particles, which restricts their motion. At this point, the bituminous phase contributes less to resisting external shearing forces, which are primarily sustained by the CR particles. This results in a sudden drop in the Black diagram.

The G-R parameter calculated for the unconditioned samples is presented in Table 5, and

the complex shear modulus and phase angle at 0.005 rad/s and 15 °C are plotted in Figure 10 alongside the G-R thresholds. All blends exhibit values well below the 180 kPa threshold limit. The addition of CR increased in the G-R parameter close to the values for PMB, which can be attributed to longer relaxation times, resulting in the accumulation of residual stresses as the binder cannot rapidly dissipate applied stresses. When compared to CRMB, the blends containing AC, GFA, and PCP showed an increase of 67%, 13%, and 19% in G-R values, respectively. For all CRMB blends, the G-R parameter shifted towards the upper left region of the graph, confirming that the addition of CR and ERA increased the vulnerability to cracking, with the blend with AC being closer to the damage zone.

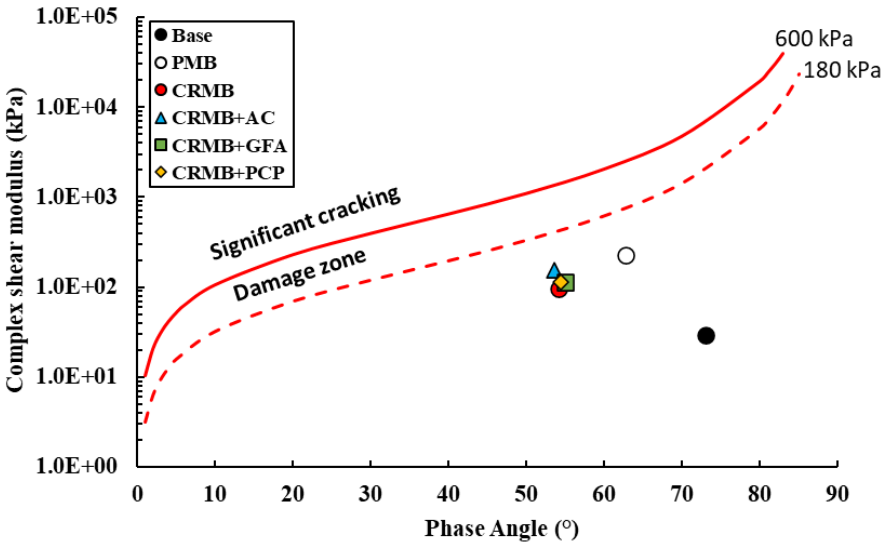


Figure 10. Complex shear modulus and phase angle at 0.005 rad/s and 15°C plotted with the G-R thresholds in a Black diagram

ΔT_c – Low temperature

Table 5 presents the results for $T_{c,G}$, $T_{c,m}$, and ΔT_c. The introduction of CR led to a significant reduction in ΔT_c, lowering it by nearly 6 °C and exceeding the critical limit of -5 °C. Surprisingly, PMB also exhibited a lower ΔT_c than the base binder, approaching the critical limit. The incorporation of CR into the base binder slightly reduced $T_{c,m,}$ with

the difference being minimal after the addition of ERAs. Conversely, the large shift in $T_{c,G}$ to colder temperatures explained the decrease in ΔT_c. Thus, although $T_{c,G}$ improved, the fact that $T_{c,m}$ stayed relatively constant and ΔT_c increased in absolute value makes it difficult to conclude if CR had a positive effect on low temperature performance. A similar trend was reported by Wititanapanit et al. [63] when comparing a control bitumen with samples modified with 3 and 7% natural rubber by weight of bitumen. The samples with ERA showed slightly warmer temperatures for $T_{c,G}$ (3.2% to 9.6%) compared to CRMB, but still colder values than the base binder.

Linear amplitude sweep (LAS) – Intermediate temperature

Table 5 summarises the strain values at failure (γ_f), the peak stored strain energy (PSE), and the number of cycles to failure ($N_{f,test}$) obtained from the LAS test. Notably, the addition of CR to the base binder increased the strain at failure by 32% and the maximum number of cycles to failure by 35%, indicating a superior fatigue performance. However, the addition of AC, GFA, and PCP reduced the performance of the CRMB as they showed lower values for γ_f and $N_{f,test}$. Of note, the CRMB+AC exhibited even inferior values than the base binder. Interestingly, PMB was the binder with the lowest γ_f and $N_{f,test}$ but with the highest PSE. An explanation to the increase in performance provided by the CR could be that the additional strain experienced beyond the peak in shear stress activated the polymer network present in CR modified binders, enhancing the binder's capacity to accumulate energy during successive loading cycles and consequently increasing the number of cycles to failure.

Rutting Resistance Indicator (MSCR test) – High temperature

The results at two stress levels (0.1 and 3.2 kPa) for the non-recoverable creep compliance

(J_{nr}) and the percent recovery (%R) are presented in Table 5. The base binder used in this study has a softening point of just 51.8 °C, rendering it unsuitable for effectively resisting plastic permanent deformation at elevated temperatures and it can clearly be seen as a high non-recoverable deformation and low recovery. The addition of CR reduced J_{nr} to around 1/4th of its original value and increased %R significantly (55% and 57% for $R_{0.1}$ and $R_{3.2}$, respectively) to values more comparable to the ones for PMB, hence possibly improving rutting resistance. The addition of ERA did not show significant changes in the values for non-recoverable deformation and percent recovery when compared to the ones for CRMB.

5. Finding and conclusions

This study investigated the effect of emission reduction agents (ERAs) on the properties of crumb rubber modified bitumen (CRMB) and compared the results with the properties of a base binder and a polymer modified binder (PMB). Firstly, it was found that the addition of crumb rubber (CR) caused an overall stiffening effect on the base binder, which was substantiated by a lower penetration, a higher softening point and penetration index, increased viscosity, and a greater activation energy. In terms of rheology, the Cole-Cole plots, master curves, and MSCR results showed a more elastic response of the binder after adding CR, particularly in the high temperature-low frequency domain. Finally, CR seemed to reduce temperature dependency and improve the fatigue resistance at intermediate temperatures but it was unclear whether there was any benefit in terms of stress relaxation at lower temperatures.

Regarding the effect of ERAs on CRMB, it was concluded that all ERAs had an additional stiffening effect: penetration reduced and softening point, penetration index, and viscosity increased. This stiffening effect caused a significant drop in the fatigue resistance

measured in the LAS test. Out of the three ERAs evaluated, AC clearly induced the greatest changes in binder properties. However, MSCR results, crossover frequency, R-value, Glower-Rowe parameter, and ΔT_c were less sensitive to the addition of ERAs.

When the results for CRMB+ERAs were compared with those for the base binder, it become evident that the incorporation of CR was the predominant factor influencing the characteristics of the modified blends, except for the LAS test, where the ERAs clearly had a strong effect on the fatigue response. When compared with the PMB, the CRMB+ERAs blends performed similarly in terms of both physical and rheological properties.

All in all, this study showed that the addition of ERAs like GFA and PCP did not impair the physical and rheological properties of CRMB, yielding results comparable to those of a PMB. However, the use of AC notably increased viscosity and worsened the fatigue response in the LAS test, which may introduce issues during mixing and service life. Future research should focus on assessing the environmental impact of CRMB with the incorporation of ERAs using life cycle assessment (LCA) to help make informed decisions about the best environmental option for CRMB production.

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