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Low-carbon bio-recycled asphalt development: Insights into the rheological and chemical behaviour of bio-rejuvenated bitumen with warm-mix additives

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ABSTRACT

This study investigates the effects of warm-mix asphalt (WMA) additives and bio-oil on the rheological and chemical properties of virgin bitumen (VB) and polymer-modified bitumen (PMB) under varying aging conditions. The workability, viscoelasticity, and chemical characteristic of warm-mix bio-rejuvenated bitumen are assessed using a rotational viscometer, dynamic shear rheometer, Fourier Transform Infrared Spectroscopy. Results show that PMB has superior aging resistance than VB. The wax-based additive exponentially reduces viscosity of VB, while the chemical-based additive decreases viscosity linearly and performs better in PMB due to improved polymer-bitumen interfacial lubrication. The wax-based additive enhances high-temperature elasticity and rutting resistance, whereas adding 0.9 wt% chemical-based additive declines the rutting failure temperature (RFT) of VB by 3.3°C and PMB by 2.3°C. However, the wax-based additive lowers the fatigue life of VB, while the chemical-based additive extends the fatigue life. The fatigue failure temperature (FFT) value increases by 2.3°C for VB and 3.4°C for PMB after adding 4 % wax-based additive. The optimal dosage of the chemical-based additive for PMB is determined to be 0.6 %. The bio-rejuvenator significantly enhances the fatigue performance of aged VB, but has limited impact on aged PMB. Both WMA additives reduce aromaticity and alter aliphatic content, with the chemical-based one showing a stronger dilutive effect, particularly in PMB. Additionally, a warm-mix bio-rejuvenated bitumen with higher aliphatic index (AlI) and carbonyl index (CI) shows better deformation resistance and longer fatigue life.

1. Introduction

The road construction industry faces growing pressure to adopt sustainable practices that minimize environmental impact while enhancing economic efficiency. Warm-mix asphalt (WMA) technology has emerged as a promising solution, significantly reducing energy consumption and greenhouse gas emissions during asphalt production and construction [1–3]. By enabling lower mixing and compaction temperatures, WMA technology not only aligns with global climate goals but also extends equipment lifespan and reduces operational costs, making it a valuable tool for modern infrastructure development [4,5]. Simultaneously, the incorporation of reclaimed asphalt pavement (RAP) has gained traction as a complementary strategy to warm-mix asphalt, promoting resource conservation and circular economy principles in road construction [6–8]. The reuse of aged bitumen from decommissioned roads minimized the demand for virgin materials and reduces the waste generated in construction projects [9,10]. This approach not only conserves natural resources but also decreases landfill use and lowers the overall environmental footprint during pavement construction and maintenance [11,12].

While WMA and RAP individually offer significant sustainable benefits, their integration poses both opportunities and challenges [13,14]. A combined approach can maximize resource efficiency while maintaining or enhancing pavement performance [15,16]. However, aged RAP bitumen, characterized by increased stiffness and brittleness, may compromise the workability and durability of WMA mixtures, particularly given the lower processing temperatures [17–19]. Addressing this issue requires innovative strategies to balance the conflicting effects of warm-mix and RAP recycling.

To facilitate the incorporation of RAP in WMA mixtures, a range of

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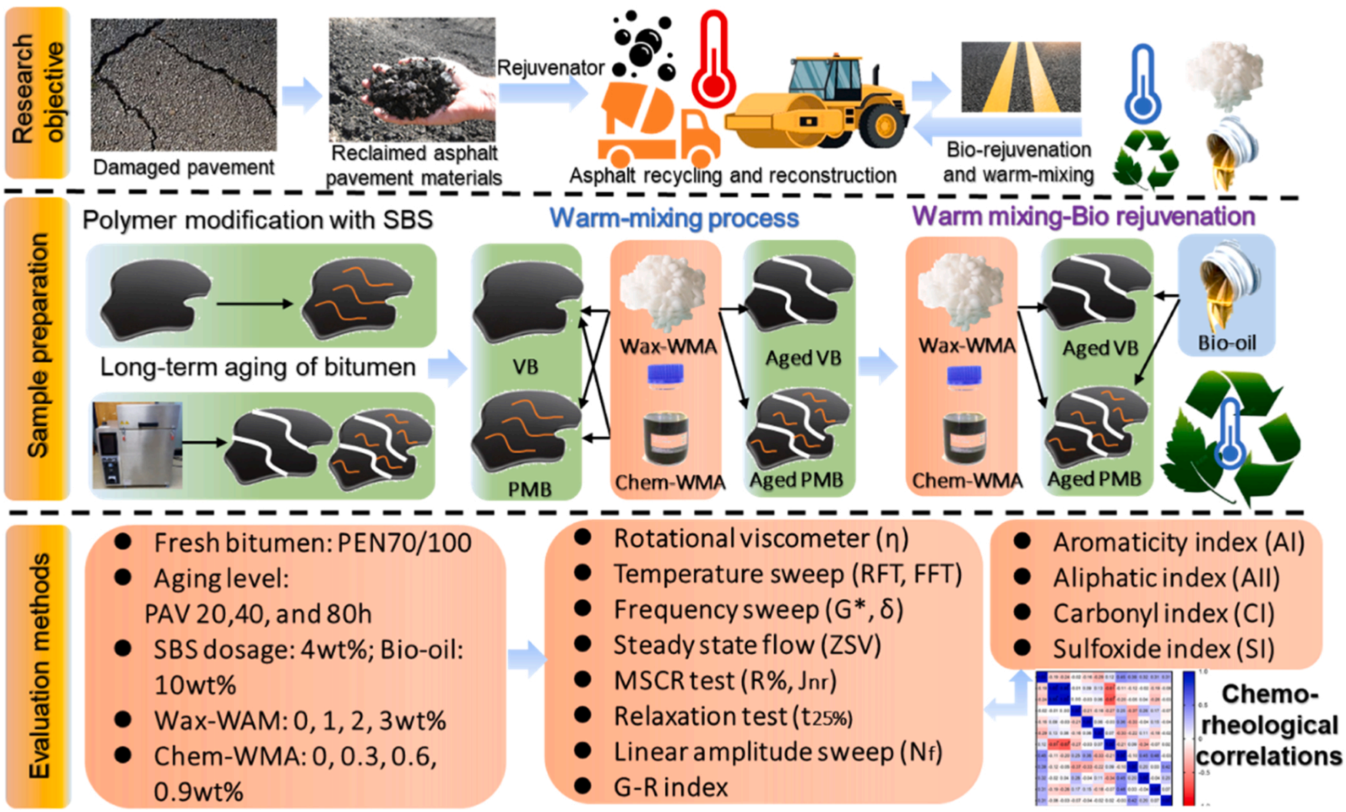

Fig. 1. The research flowchart of this study.

warm-mix additives has been developed [20,21]. These additives, including wax-based and chemical-based agents, function through distinct mechanisms to reduce viscosity and improve bitumen compatibility [22–24]. However, increasing RAP content in WMA mixtures can negatively affect key properties such as fatigue and moisture resistance. Therefore, effective mitigation strategies, including the use of recycling agents, are essential to counteract these drawbacks [25,26]. Bio-based recycling agents, derived from renewable sources, offer a promising solution by replenishing essential bitumen components lost during aging, thereby improving both sustainability and performance [27]. The synergistic use of warm-mix additives and bio-rejuvenators aims to optimize both workability and long-term durability in recycled asphalt mixtures.

Despite the growing adoption of WMA and RAP technologies, the performance of warm-mix recycled mixtures remains influence by a complex interplay of multiple variables. These include the type of bitumen used (virgin bitumen or polymer modified bitumen), each of which responds differently to aging and modification processes [28]. The degree of aging in RAP binder alters its chemical structure and rheological properties, playing a critical role in determining the compatibility and performance of the recycled mixtures [29,30]. Moreover, the type and dosage of WMA additive significantly affect mixture workability, viscosity reduction, and overall mechanical performance, as these additives function via distinct mechanisms such as viscosity reduction, surface tension modification, and polymer interaction [31,32]. The efficacy of recycling agents, particularly bio-based rejuvenators, also varies depending on their chemical composition and interaction with both aged bitumen and additives [33]. Therefore, a comprehensive and systematic understanding of these independent variables is essential to formulate high-quality rejuvenated bitumen that balance workability, stiffness, durability, and sustainability for long-term pavement performance.

In this context, exploring the chemical and rheological properties of bitumen and polymer-modified bitumen modified with WMA additive and bio-rejuvenators under different conditions is essential, particularly in light of recent finding showing that rubber-polymer composite formulations can enhance softening temperature and resistance to plastic deformation [34]. A deeper understanding of these interactions can help identify mechanisms that ensure the performance of recycled asphalt mixtures while advancing sustainability goals. This study seeks to address the following key research gaps: (i) limited work has comprehensively evaluate the effect of different WMA additives on viscosity reduction and chemo-mechanical properties of aged bitumen and aged-PMB, (ii) The combination of warm-mix and bio-rejuvenation on aged bitumen has not been studied yet, (iii) The chemo-mechanics of warm-mix rejuvenated bitumen are still unclear.

2. Research objective and structure

This research aims to explore the potential combination of warm-mix and bio-rejuvenation technologies for the green and sustainable recycling of RAP materials through investigating the effects of WMA additives on virgin, aged, and bio-rejuvenated bitumen. As shown in Fig. 1, It is expected to decrease the mixing and compaction temperatures during the bio-recycling process. Two WMA additives, wax-based and chemical-based, are added to bitumen and polymer-modified bitumen (PMB) before and after long-term aging. The influence factors of WMA additive type/dosage, polymer, aging degree of bitumen are considered. Viscosity measurements are conducted using a rotational viscometer, while Fourier Transform Infrared Spectroscopy (FTIR) is utilized to assess functional group distribution. Additionally, the dynamic shear rheometer (DSR) is used to characterize viscoelastic behavior, high-temperature rutting, low-temperature relaxation, and fatigue performance of warm-mix bio-rejuvenated bitumen through frequency sweep, temperature sweep, multiple stress creep and recovery (MSCR), stress relaxation, and linear amplitude sweep (LAS) tests. Lastly, chemo-rheological correlations are analysed to optimize the chemical components of WMA additives for different virgin, aged, and bio-rejuvenated

Table 1
Chemo-physical properties of virgin bitumen [37].

Properties	Value	Test Standard
25°C penetration (0.1 mm)	91	ASTM D5 [38]
Softening point (°C)	48	ASTM D36 [39]
135°C dynamic viscosity (Pa·s)	0.8	AASHTO T316 [40]
25°C density ($g\cdot cm^3$)	1.017	EN 15326 [41]
60°C density ($g\cdot cm^3$)	0.996	
Saturate fraction, S (wt%)	3.6	ASTM D4124 [42]
Aromatic fraction, A (wt%)	53.3	
Resin fraction, R (wt%)	30.3	
Asphaltene fraction, As (wt%)	12.8	
Carbon, C (wt%)	84.06	ASTM D7343 [43]
Hydrogen, H (wt%)	10.91	
Oxygen, O (wt%)	0.62	
Sulphur, S (wt%)	3.52	
Nitrogen, N (wt%)	0.9	

Table 2
Basic properties of WMA additives and bio-rejuvenator [44,45].

Properties	Wax-based	Chemical-based	Bio-oil
Physical state and color	Pastille flakes, off-white	Liquid, dark brown	Liquid, pale yellow
Appearance			
25°C Density (g/cm^3)	0.900	0.992-	0.911
20°C Solubility in water	Insoluble	Soluble	Limited soluble
25°C Viscosity (cP)	-	374	50
40°C Viscosity (cP)	-	216	30
40°C Density (g/cm^3)	-	0.962	0.905
Flash pint (°C)	285	230	265–305
Initial boiling point (°C)	271	215	175–230

bitumen with and without polymer modification.

3. Materials and methodology

3.1. Materials

A 70/100 penetration-grade bitumen was selected, with its fundamental properties summarized in Table 1. To produce the warm-mix bitumen, two commercial WMA additives (wax-based and chemical-based) were used. The key characteristics of these WMA additives and the bio-oil are provided in Table 2. The main molecular components of the bio-rejuvenator are methyl oleate, methyl linoleate, and methyl palmitate [35]. In addition, one Styrene-Butadiene-Styrene (SBS)-modified bitumen was prepared using 70/100 penetration-grade bitumen as the base bitumen, incorporating 4 % by weight of Kraton D1102 SBS. This SBS polymer is a linear block copolymer comprising 28.5 % styrene [36]. It is important to note that virgin bitumen is abbreviated as VB, while SBS-modified bitumen is referred to as PMB.

3.2. Aging of virgin and modified bitumen

In this study, both virgin and SBS-modified bitumen underwent short-term and long-term laboratory aging to produce aged bitumen. The samples were aged using the Thin-Film Oven Test (TFOT) and the Pressure Aging Vessel (PAV). The TFOT was conducted at a temperature of 163°C for a duration of 5 h. The PAV aging process was carried out at 100°C and a pressure of 2.1 MPa, with aging times set at 20 h, 40 h, and 80 h to examine the influence of aging degrees [37]. The aged bitumen samples were designated as 1 P, 2 P, and 4 P, while the aged SBS-modified bitumen samples were labelled 1PM, 2PM, and 4PM.

3.3. Preparation of WMA bitumen and warm-mix bio-rejuvenated bitumen

Both virgin bitumen and SBS-modified bitumen were heated in an oven at 140°C to ensure proper flowability. Subsequently, the WMA additive was incorporated into bitumen. The wax-based additive was added at dosages of 0 %, 1 %, 2 %, and 4 % by weight of bitumen, while the chemical-based additive was introduced at concentrations of 0 %, 0.3 %, 0.6 %, and 0.9 %. To obtain homogeneous warm-mix bitumen, the bitumen and additives were blended thoroughly using a high-speed mixer with a shear rate of 1500 rpm at 140°C for 30 min. The aged bitumen and aged SBS-modified bitumen were first mixed with 4 % wax-based additive at 140°C for 30 min. Subsequently, a bio-oil (10 wt%) was added to prepare the warm-mix bio-rejuvenated bitumen with blending time of 10 min at 140°C [48]. To simplify, the abbreviations for all samples are summarized in Table 3.

3.4. Characterization methods

3.4.1. Viscosity test

The dynamic viscosity of all bitumen was measured using a rotational viscometer (Brookfield DV2T) in accordance with the AASHTO T316–13 standard [40]. The testing was conducted at variable temperatures of 100°C, 110°C, 120°C, 135°C, and 150°C. The rotor operates at

Table 3
List of abbreviations for all samples in this study.

VB	Aging time (h)	Wax-WMA (wt%)	Chem-WMA (wt%)	Bio-oil (wt%)	**PMB**	Aging time (h)	Wax-WMA (wt%)	Chem-WMA (wt%)	Bio-oil (wt%)
S1	0	1	-	-	MS1	0	1	-	-
S2	0	2	-	-	MS2	0	2	-	-
S3	0	4		-	MS3	0	4		-
C1	0	-	0.3	-	MC1	0	-	0.3	-
C2	0	-	0.6	-	MC2	0	-	0.6	-
C3	0	-	0.9	-	MC3	0	-	0.9	-
1 P	20	-	-	-	1PM	20	-	-	-
2 P	40	-	-	-	2PM	40	-	-	-
4 P	80	-	-	-	4PM	80	-	-	-
1PS	20	4	-	-	1PMS	20	4	-	-
2PS	40	4	-	-	2PMS	40	4	-	-
4PS	80	4	-	-	4PMS	80	4	-	-
1PSB	20	4	-	10	1PMSB	20	4	-	10
2PSB	40	4	-	10	2PMSB	40	4	-	10
4PSB	80	4	-	10	4PMSB	80	4	-	10

a fixed spinning rate of 20 rpm.

3.4.2. Frequency and temperature sweep test

In this study, the frequency sweep tests were performed with dynamic shear rheometer (DSR) on fresh, aged, and bio-rejuvenated bitumen to evaluate their viscoelastic properties, including the complex modulus (G*) and phase angle (δ) at 20°C. These tests covered a frequency range from 0.1 rad/s to 100 rad/s with a strain level of 0.2 %. Additionally, temperature sweep tests were carried out at a constant frequency of 10 rad/s, with the temperature increasing from 0°C to 50°C in 10°C increments [46].

3.4.3. Multiple stress creep and recovery (MSCR) test

The MSCR test was performed at two stress levels (0.1kPa and 3.2kPa) at 58°C. Each test consisted of ten cycles, with a total duration of 200 s per stress level. During each cycle, the bitumen sample experienced a 1 s creep phase followed by 9 s recovery phase. The strain-time response was recorded to compute two essential rheological indices: the recovery percentage R (%) and the recoverable creep compliance J_{nr} (kPa^{-1}), defined by the following equations:

$$R(\sigma, N) = \frac{\varepsilon_c - \varepsilon_r}{\varepsilon_c - \varepsilon_0} \times 100 \tag{1}$$

$$J_{nr}(\sigma, N) = \frac{\varepsilon_r - \varepsilon_c}{\sigma} \tag{2}$$

where δ represents the applied stress (kPa), and N refers to the creep/recovery cycles, ε_0(%) denotes the initial shear strain during the creep phase, while ε_c (%) and ε_r (%) are the shear strain values at the end of the creep and recovery phases, respectively. It is worth noting that the R index reflects the elastic recovery, while the J_{nr} parameter indicates its deformation potential.

3.4.4. Relaxation test

The impacts of WMA additives and bio-rejuvenator on the low-temperature performance of VB and SBS-modified bitumen was assessed through a relaxation test at 0°C in strain-controlled mode. The strain level was set at 1 %, and the relaxation process comprised two distinct phases: an initial strain-loading phase (lasting from 0 to 0.1 s) and a constant-strain phase (extending from 0.1 to 100 s). During the loading phase, the strain was progressively increased from 0 % to 1 %, reaching the target strain within the specified timeframe. Key evaluation metrics, including the shear stress at 50 s ($\tau_{50\ s}$) and the relaxation time corresponding to a 25 % reduction in stress ($t_{25\ \%}$), were recorded and analysed [47].

3.4.5. Glover-Rowe (G-R) and Linear amplitude sweep (LAS) test

To evaluate the fatigue performance, the linear viscoelastic parameter G-R was calculated using Eq.3, where G* represents the complex modulus and δ denotes the phase angle, both measured at 0.005 rad/s and 15°C:

$$G - R = \frac{|G^*|(\cos\delta)^2}{\sin\delta} \tag{3}$$

Furthermore, the LAS tests were performed on all bitumen samples. During the LAS test, the applied strain increased linearly from 0.1 % to 30 %, with the temperature set at 25°C and the frequency at 10 Hz. The test included 3100 loading cycles, spanning a total duration of 310 s. The results of the LAS tests were interpreted using the Simplified Viscoelastic Continuum Damage (S-VECD) model [47], which introduces an internal damage parameter (S) to quantify the extent of deterioration in bituminous materials:

$$\frac{ds}{dt} = \left(-\frac{\partial W^R}{\partial S}\right)^\alpha \tag{4}$$

where α is a material constant representing the damage progression rate, t is the fatigue time, and W^R is the pseudo-strain energy density calculated as:

$$W^R = \frac{1}{2}C(S)(\gamma^R)^2 \tag{5}$$

The function C(S) represents the pseudo stress and serves as a measure of material integrity. It is expressed as the ratio of peak stress (τ_P) to pseudo strain amplitude (γ^R), which is further defined as:

$$\gamma^R = \frac{(\gamma_P \bullet G^*_{LVE})}{G_R} \tag{6}$$

where γ^R denotes the strain amplitude during a fatigue cycle, and G_R and G^*_{LVE} are the reference modulus and linear viscoelastic shear modulus, respectively. The damage parameter S can be derived as follows, where N represents the total number of load cycles, and i denotes a specific cycle:

$$S = \sum_{i=1}^{N} \left[\frac{1}{2}(\gamma^R)^2(C_{i-1} - C_i)\right]^{\frac{\alpha}{\alpha+1}} \bullet \quad (t_i - t_{i-1})^{\frac{1}{\alpha+1}} \tag{7}$$

The relationship between material integrity C and damage S is modelled with a power law:

$$C(S) = 1 - C_1 \bullet S^{C_2} \tag{8}$$

Using these equations, the fatigue life (N_f) of bitumen can be expressed as a function of strain amplitude (γ_P) as follows:

$$N_f = \frac{f \bullet 2^\alpha \bullet S_f^{1-\alpha C_2+\alpha}}{(1 - \alpha C_2 + \alpha)(C_1 C_2)^\alpha (\gamma_p \bullet G^*_{LVE})^{2\alpha}} \tag{9}$$

where f is the fatigue loading frequency, and S_f denotes the damage at the failure point as Eq.10:

$$S_f = \left(\frac{1 - C_f}{C_1}\right)^{\frac{1}{C_2}} \tag{10}$$

Here, C_f denotes the integrity value at failure, corresponding to the peak stress. For simplicity, N_f can be reformulated as below, where B= -2α, and k = 1-αC_2+ α.

$$N_f = A \bullet (\gamma_p)^B \tag{11}$$

$$A = \frac{f \bullet 2^\alpha \bullet S_f^k}{k(C_1 C_2)^\alpha (G^*_{LVE})^{2\alpha}} \tag{12}$$

3.4.6. Fourier Transform Infrared Spectroscopy (FTIR) test

The chemical functional groups of all bitumen were examined using a PerkinElmer ATR-FTIR spectrometer equipped with a single-point ATR attachment. Each sample was scanned across a wavenumber range of 600–4000 cm^{-1}, with 12 scans performed per sample at a fixed resolution of 4 cm^{-1}. To improve the accuracy of the results, each sample was tested in triplicate.

To quantitatively assess the effects of WMA additives and bio-rejuvenator on chemical characteristics, the aromaticity index (AI), aliphatic index (AII), carbonyl index (CI) and sulfoxide index (SI) were calculated as follows [48]:

$$AI = \frac{A_{1600}}{\sum A} \tag{13}$$

$$AII = \frac{A_{1460} + A_{1375}}{\sum A} \tag{14}$$

$$CI = \frac{A_{1700}}{\sum A} \tag{15}$$

$$SI = \frac{A_{1030}}{\sum A} \tag{16}$$

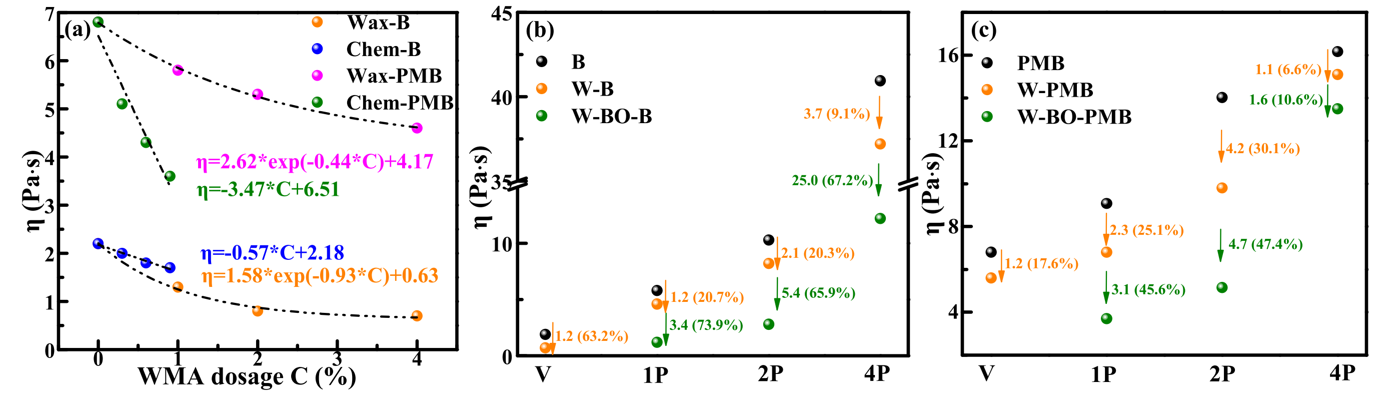

Fig. 2. Viscosity variation of warm-mix bio-rejuvenated bitumen.

$$\sum A = A_{(2952,\quad 2862)} + A_{1700} + A_{1600} + A_{1460} + A_{1375} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} \tag{17}$$

where A_{1700}, A_{1600}, A_{1460}, A_{1375}, and A_{1030} is the peak area of absorption peat when the wavenumber is 1700, 1600, 1460, 1375, and 1030 cm^{-1}, respectively. Additionally, the $\sum A$ refers to the total area of all absorption peaks.

4. Results and discussion

4.1. Viscosity

The viscosity changes in VB and PMB with wax-based and chemical-based WMA additives are plotted in Fig. 2. Increasing the dosage of both WMA additives clearly results in a significant decrease in viscosity, thereby enhancing workability at reduced temperatures. For both VB and PMB, their viscosity exhibits a linear decline as the chemical-based additive dosage increases, whereas an exponential decline trend is observed for wax-based one. Notably, wax-based additive proves more effective than the chemical-based one in producing a pronounced reduction in the viscosity of VB. Wax-based one is mainly composed of straight chain alkanes as saturate fraction, and the chemical-based one is to reduce the interfacial tension [22]. As expected, PMB exhibits higher viscosity than VB due to the inclusion of SBS polymer. Chemical-based additive proves more effective than wax-based additive in lowering viscosity of PMB, related to a significant reduction of interfacial tension force between polymer and bitumen. While the wax-based additive reduces viscosity of PMB, its impact is less pronounced compared to its effect on VB. Consequently, the wax-based additive is better suited for WMA with VB, whereas chemical-based additive is more advantageous

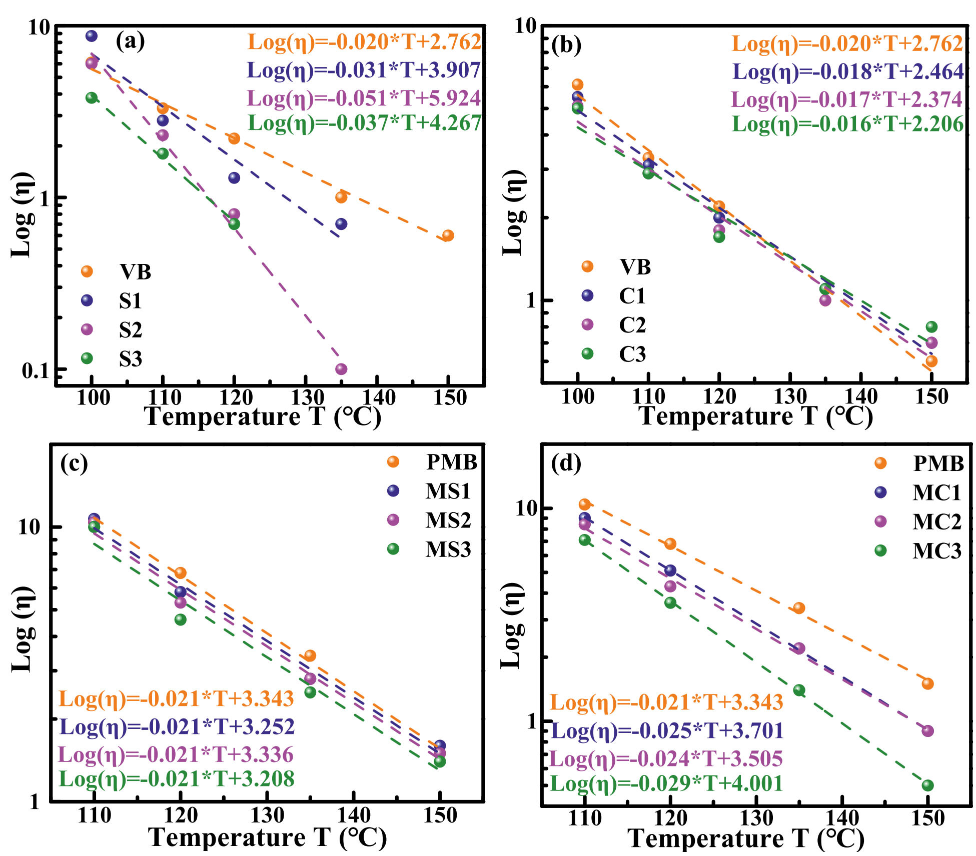

Fig. 3. Temperature sensitivity of VB and PMB with WMA additives.

Table 4
Mixing and compaction temperatures of different warm-mix bitumen.

Samples	T_m(°C)	T_c(°C)	Slope	Intercept	Samples	T_m(°C)	T_c(°C)	Slope	Intercept
VB	175	164	−0.020	2.734	PMB	196	186	−0.021	3.343
1 P	179	171	−0.028	4.239	1PMB	186	178	−0.026	4.078
2 P	183	176	−0.030	4.724	2PMB	184	177	−0.031	4.952
4 P	206	199	−0.033	6.024	4PMB	188	181	−0.030	4.879
VBS	136	130	−0.037	4.267	PMBS	191	181	−0.022	3.432
1PS	169	161	−0.031	4.463	1PMS	184	175	−0.025	3.824
2 PS	176	169	−0.032	4.849	2PMS	182	174	−0.031	4.858
4 PS	201	193	−0.028	4.852	4PMS	189	182	−0.029	4.713
1PSB	163	156	−0.030	4.124	1PMSB	169	161	−0.030	4.289
2PSB	168	161	−0.031	4.458	2PMSB	170	163	−0.033	4.831
4PSB	189	182	−0.029	4.713	4PMSB	175	168	−0.032	4.825

for use with PMB.

From Fig. 2(b) and (c), the viscosity of VB rises sharply with prolonged aging, indicating significant hardening caused by oxidation, especially after extended periods such as 80 h [48]. This pronounced increase highlights the high aging sensitivity of VB, compromising its flexibility and increasing cracking potential [25]. In contrast, PMB shows a more gradual viscosity increase. In detailed, PMB exhibits a higher viscosity (6.8 Pa·s) than virgin bitumen, and its viscosity only rises to 16.2 Pa·s even after 80 h aging. This demonstrates the improved aging resistance of PMB, likely attributable to the stabilizing effects from polymers [49]. For aged VB and PMB, both wax-based additive and bio-oil effectively lower the viscosity, with bio-oil showing a greater efficiency. For 4P-aged VB, the wax-based additive achieves only a 9.1 % reduction in viscosity due to the limited content. In constrast, the wax-based additive becomes relatively more effective in 4P-aged PMB than aged VB, which may related to the change in bitumen-polymer interaction with the existence of wax-based additive. For aged VB and PMB, the bio-oil demonstrates superior effectiveness in restoring their workability, making it a highly promising option for rejuvenating severly aged bitumen. Based on viscosity reduction degrees, bio-oil has a more pronounced impact on aged VB compared to aged PMB.

4.2. *Temperature sensitivity*

A linear relationship between Log(η) and temperature (T) is observed, with the corresponding correlation equations displayed in Fig. 3. The slope values of these equations indicate the temperature sensitivity, where a higher absolute slope corresponds to stronger temperature sensitivity. For VB, the wax-based additive increases temperature sensitivity, attributed to the high-temperature susceptibility of its wax component. Conversely, the chemical-based additive reduces temperature sensitivity, as the liquid chemical component remains relatively stable at high temperatures. Interestingly, wax-based additive has no measurable effect on temperature sensitivity of PMB, while chemical-based additive increases it. It is the opposite of its effect on VB, highlighting the necessity of selecting WMA additives considering the bitumen type, as the optimal additive for VB may not yield similar benefits for PMB.

Table 4 summarizes the slope and intercept values from the Log(η)-T correlation equations for all samples. The WMA additives consistently reduce the temperature sensitivity of the bitumen. The intercepts increase as aging and polymer modification, and WMA additives lower the viscosity, even for aged-PAB samples. Mixing and compaction

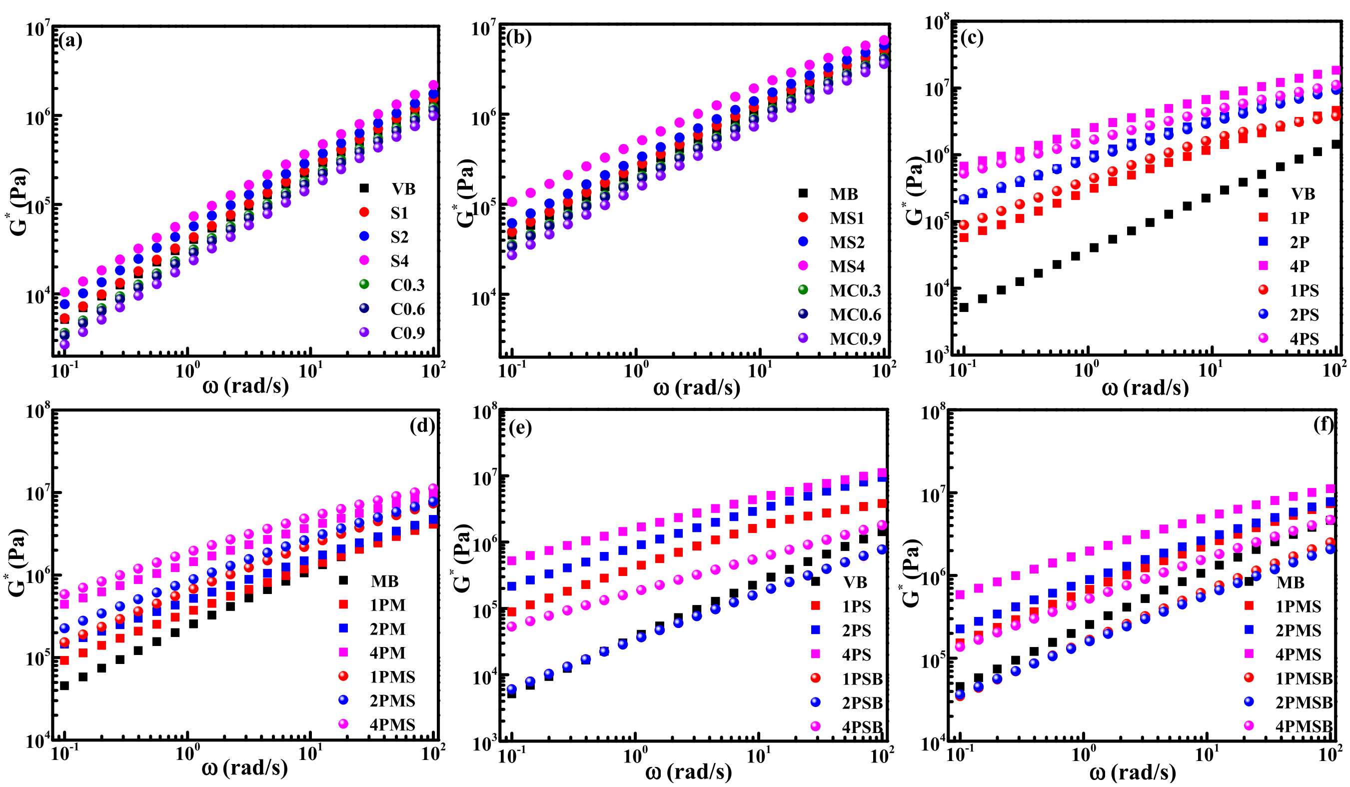

Fig. 4. Complex modulus G* of warm-mix rejuvenated bitumen at 20°C.

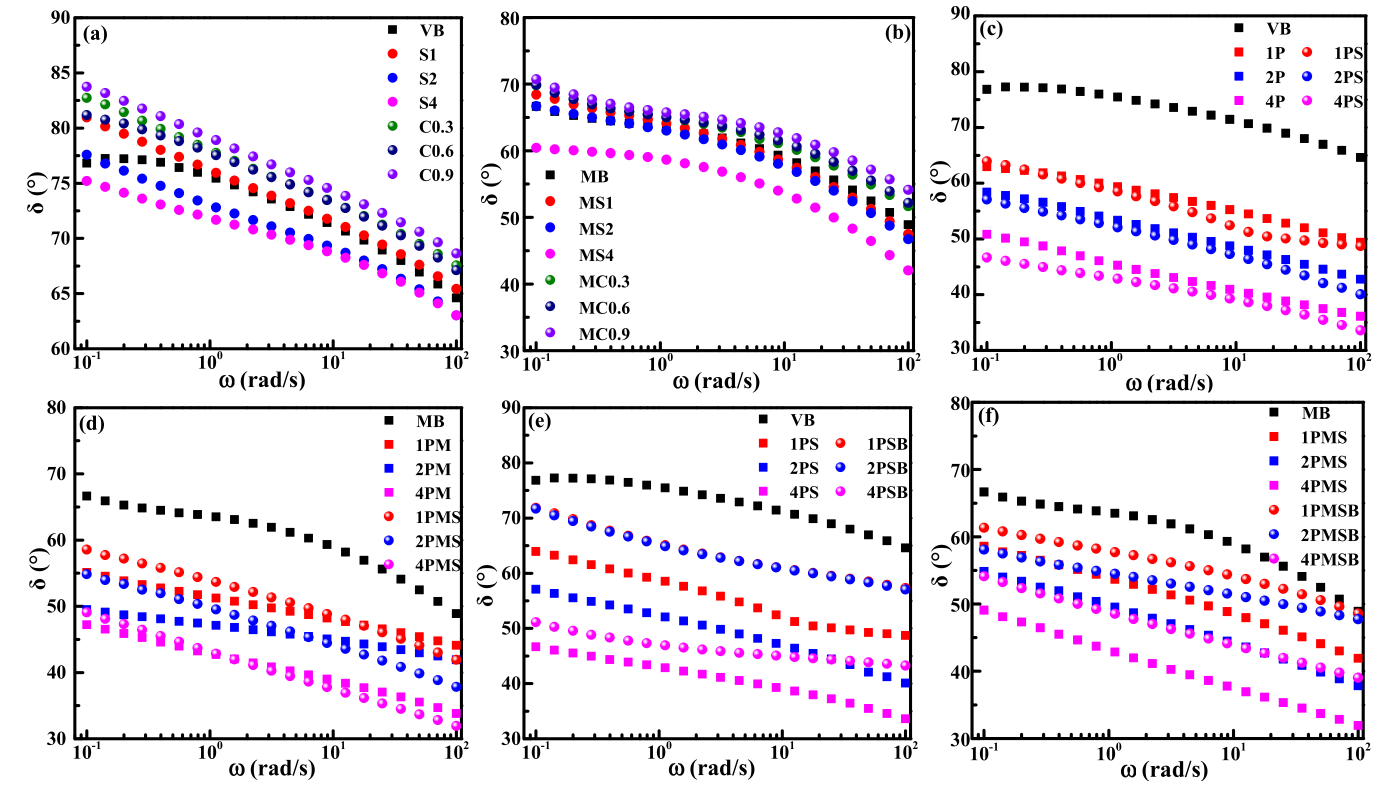

Fig. 5. Phase angle δ of warm-mix rejuvenated bitumen at 20°C.

temperatures of these bitumen are calculated based on the Superpave mixture design manual, in which the mixing and compaction temperatures are selected to correspond with bitumen viscosities of 0.17 ± 0.02 and 0.28 ± 0.03 Pa·s [49]. The polymer modification and aging results in a significant increase in mixing and compaction temperature, while the PMB shows lower T_m and T_c values than VB due to its superior aging resistance. The addition of wax-based additive reduces the T_m and T_c values firstly, and the bio-rejuvenator further decline the mixing and compaction temperature of both VB and PMB. It demonstrates that WMA additive and bio-rejuvenator display synergistic effect on lowering the mixing and compaction temperatures for RAP recycling.

4.3. Viscoelastic performance

Fig. 4 illustrates the complex modulus (G*) of the warm-mix rejuvenated bitumen for VB and PMB. The frequency-dependent behavior of G* index highlights the viscoelastic nature of the bitumen, with increased stiffness observed at higher loading frequencies. The PMB consistently exhibits higher G* values than VB, indicating superior stiffness and deformation resistance due to the elastic polymer network [23]. The G* values of VB and PMB increase after adding wax-based additive, which is more pronounced in VB and attributed to the wax crystallization. Overall, the wax-based additive reinforces stiffness and enhances resistance to high-temperature deformation of bitumen, while the chemical-based one shows a softening effect. Aging significantly increases G* values, reflecting bitumen stiffening caused by oxidation, and the increasing rate in G* for VB is notably higher than for PMB, highlighting the superior aging resistance of PMB. The wax-based additive consistently increases G* values in aged PMB, with higher dosages resulting in greater enhancements. This suggests that the wax-based additive work synergistically with the elastic polymer network in PMB, further enhancing its stiffness and high-temperature performance [28]. However, in the heavily aged bitumen (2 P and 4 P), G* values either stabilize or decrease, revealing that the softening effect of the wax-based additive becomes dominant at higher aging levels.

Fig. 4(e) and (f) demonstrate that the incorporation of 10 wt% bio-rejuvenator effectively reduces G* values of aged VB and PMB partially. For warm-mix aged-VB, bio-rejuvenator restores G* close to those of fresh VB when aging levels are 1 P and 2 P, while 4P-aged VB still retains higher modulus with a requirement of more bio-oil added. In aged PMB, less bio-oil is required to rejuvenate aged PMB with aging levels of 1 P and 2 P. However, for 4P-aged PMB, a higher bio-oil dosage would be needed to fully restore its stiffness. The results suggest that the combination of the wax-based additive and the bio-oil offers a practical solution for achieving dual objectives: enhancing stiffness for high-temperature performance while simultaneously restoring aged bitumen to mitigate the effect of oxidation and aging.

Fig. 5 illustrates the phase angle (δ) across various frequencies, offering insights into the viscoelastic behaviour different warm-mix rejuvenated bitumen. The phase angle serves as an indicator of the balance between viscous-dominant behavior and lower values indicating greater elasticity. As shown in Fig. 5(a) and (b), the δ values of VB and PMB decrease as frequency increasing, reflecting a transition from viscous behavior at low frequencies to elastic behavior at high frequencies. The δ values of PMB are consistently lower than those of VB, showcasing an improvement in elasticity introduced by the polymer. The wax-based additive consistently reduces δ values of VB and PMB and enhances their elasticity. This effect intensifies with increasing additive dosage, implying the stiffening influence of the wax-based additive. Notably, the reduction in δ values is more pronounced for PMB than for VB, suggesting a synergistic interaction between wax and the polymer network and enhanced elastic properties of PMB [50]. Conversely, the chemical-based additive increases δ values, indicating a shift toward viscous-dominant behavior due to its low viscosity and liquid characteristics.

Fig. 5(c) and (d) explore the impact of wax-based additive on δ values of aged-VB and aged-PMB. Aging significantly lowers δ values, particularly for VB, indicating increased stiffness and enhanced elastic behavior due to oxidation and molecular restructuring. However, the reduction in δ is less pronounced for PMB, signifying its superior aging

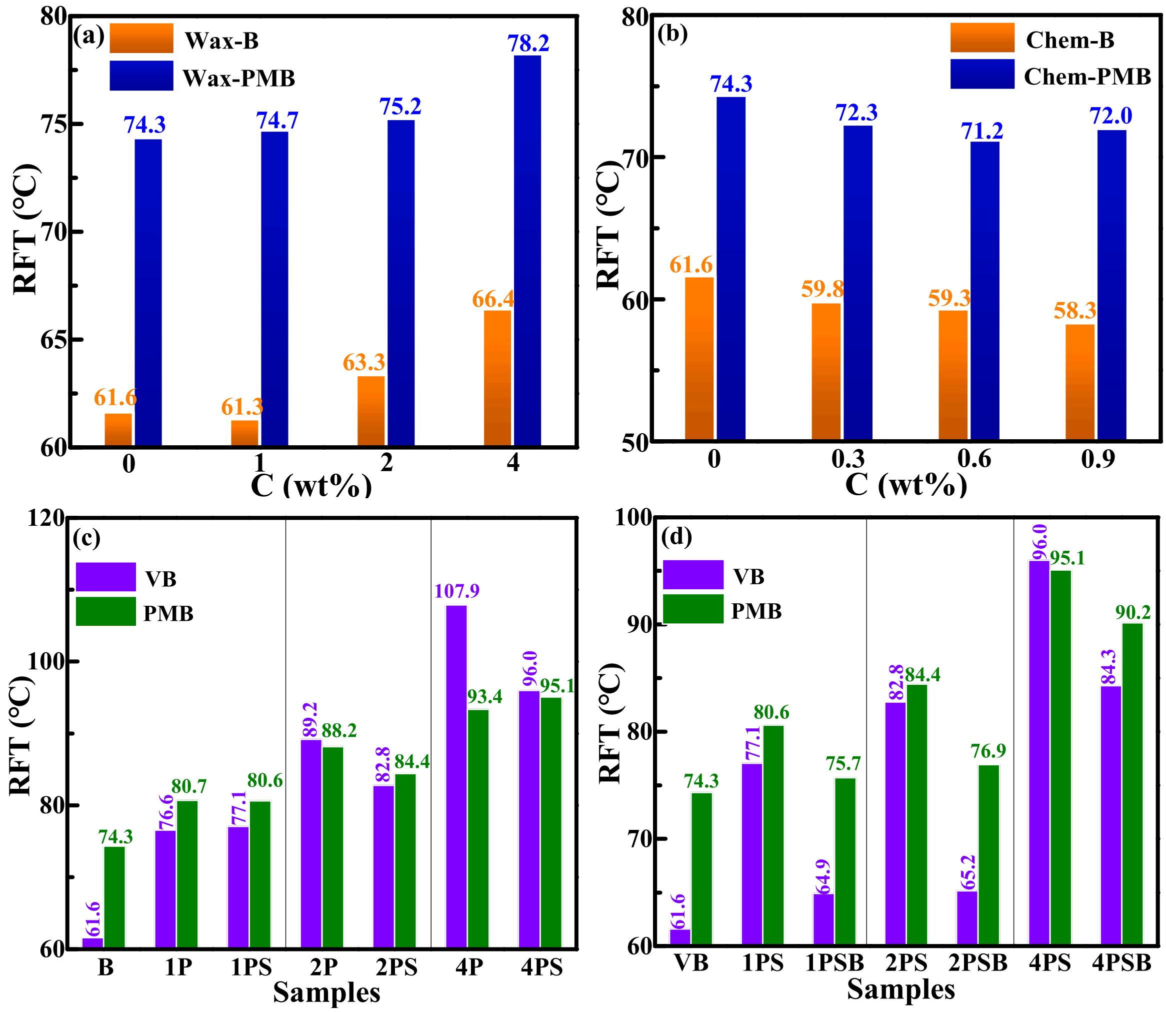

Fig. 6. Rutting failure temperature RFT of warm-mix rejuvenated bitumen.

resistance. The inclusion of the wax-based additive further reduces δ values in aged VB, highlighting its ability to enhance elastic components of aged VB, likely due to its crystallization effect. Interestingly, for aged PMB, the wax-based additive exhibits a dual effect: δ values increase at low frequencies but decrease at high frequencies. This phenomenon can be attributed to the synergistic effects of frequency, polymer interactions, and wax crystallization. At low frequencies, the polymer network inhibits wax crystallization, leading to more pronounced viscous behavior of the wax molecules [28]. In contrast, at high frequencies, the alignment and orientation effects promote wax crystallization, thereby increasing elasticity. Moreover, the aging level influences the transition frequency where the effect of wax-based additive shifts, with this transition moving to lower frequencies as the aging level increases. This behavior suggests that polymer degradation during aging reduces its hindrance to wax crystallization, allowing the wax-based additive to enhance the elastic components of aged PMB more effectively [32].

The influence of bio-rejuvenator on δ values of warm-mix aged-VB and PMB is depicted in Fig. 5(e) and (f). The bio-oil notably increases δ values, especially for heavily aged bitumen (4 P), signifying partial restoration of viscous behavior and flexibility. For VB, 10 wt% bio-oil brings δ values closer to those of fresh VB, although complete restoration is not achieved across all aging levels. For PMB, bio-oil also increases δ values but preserves an appropriate balance between viscous and elastic properties, which is essential for maintaining high-temperature performance [36]. This behavior demonstrates the efficacy of bio-oil in mitigating aging-induced stiffness while retaining the structural stability provided by polymer modification. In summary, wax-based additive and bio-oil play complementary roles in adjusting the viscoelastic behavior of aged-VB and PMB. The wax-based additive primarily enhances elasticity and stiffness, whereas the bio-oil restores viscous behaviour and flexibility.

4.4. High-temperature performance

4.4.1. Rutting failure temperature RFT

A higher RFT value signifies improved high-temperature rutting resistance in bitumen, and the RFT values of all bitumen samples are presented in Fig. 6. The RFT values of all PMB samples are at least 10°C higher than VB, attributed to the reinforcing effect of the SBS polymer. For VB and PMB, the wax-based additive increases their RFT values and enhances rutting resistance capacity. However, the chemical-based one shows a detrimental effect. From Fig. 6(c), RFT values of VB and PMB increase significantly during the long-term aging from 1 P to 4 P. Notably, the increasing rate in RFT value of VB is more significant than PMB. At aging levels 2 P and 4 P, the aged-VB even surpasses aged-PMB in RFT values, which is attributed to the aging resistance of PMB and the degradation of the SBS polymer.

The impact of the wax-based additive on aged bitumen differs from their effect on virgin bitumen, depending on aging degree and polymer existence. For VB, the WMA additive increases RFT value for 1P-aged bitumen but decreases it for 2 P and 4P-aged bitumen. This behavior may stem from variations in the chemical composition of bitumen at different aging stages [48]. In VB or 1P-aged VB, the wax-based additive

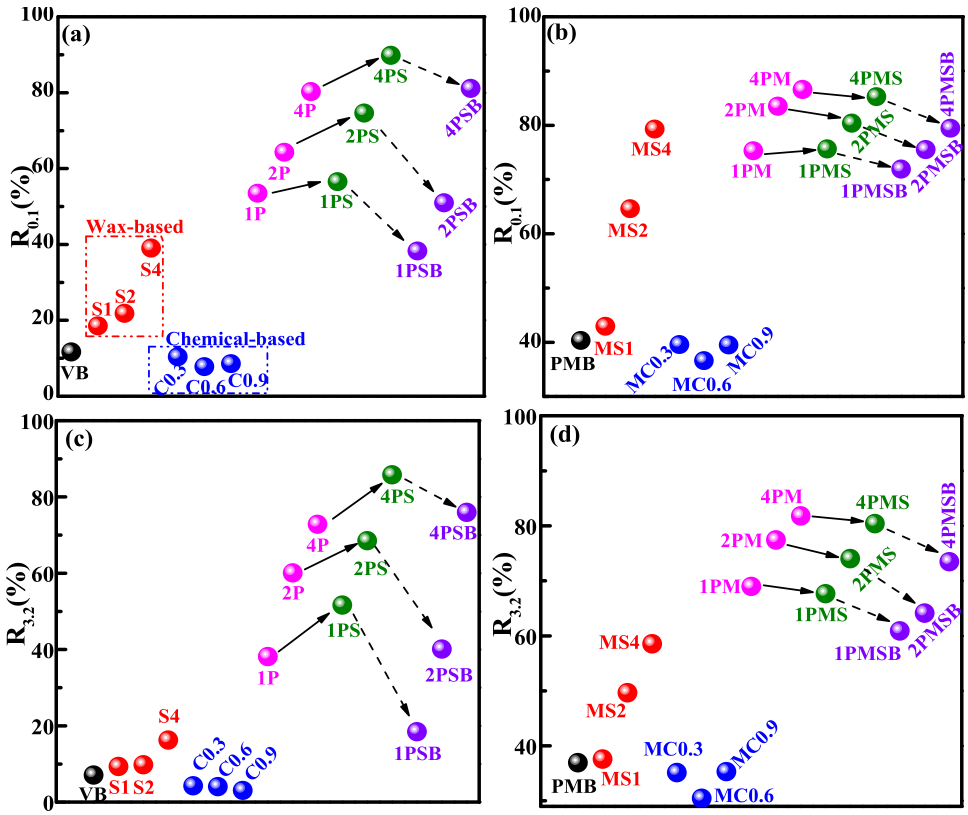

Fig. 7. $R_{0.1}$ and $R_{3.2}$ values of warm-mix rejuvenated bitumen.

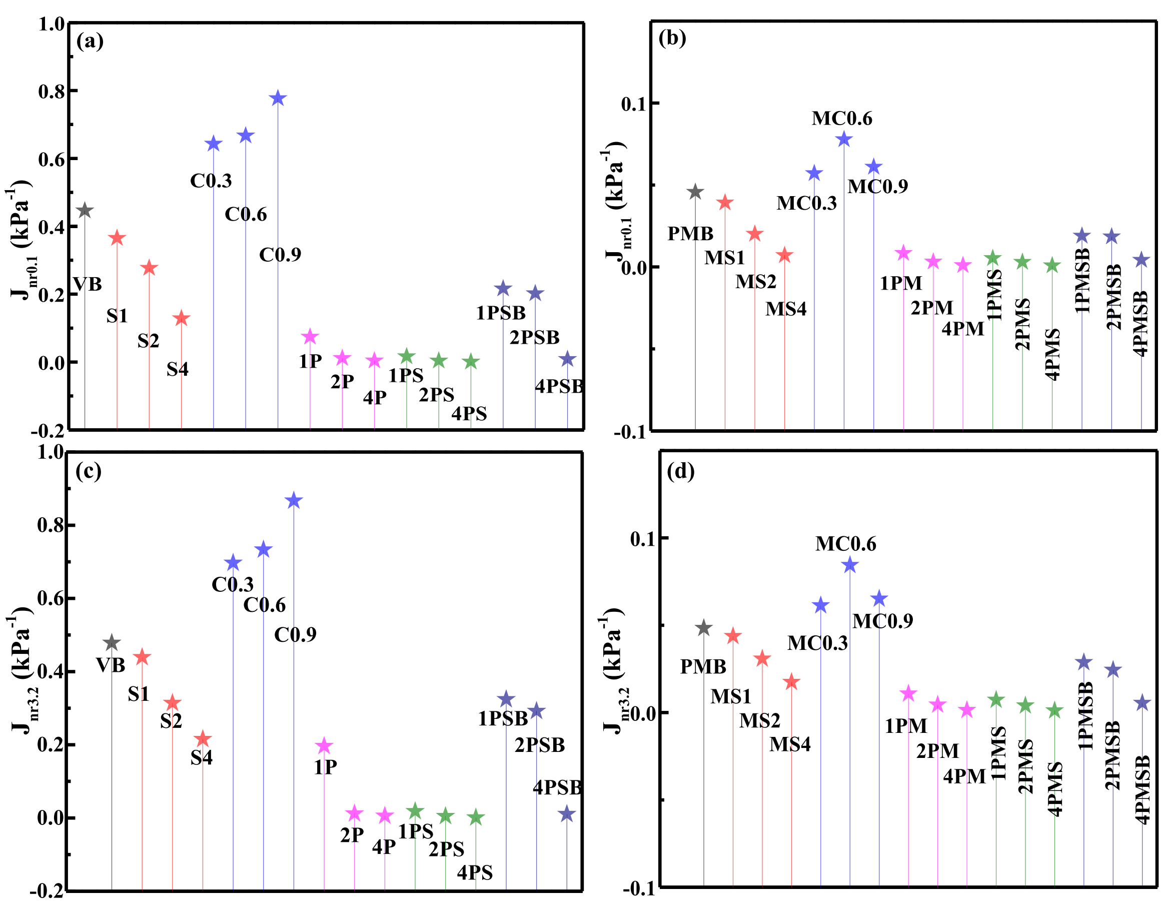

Fig. 8. $J_{nr0.1}$ and $J_{nr3.2}$ values of warm-mix rejuvenated bitumen.

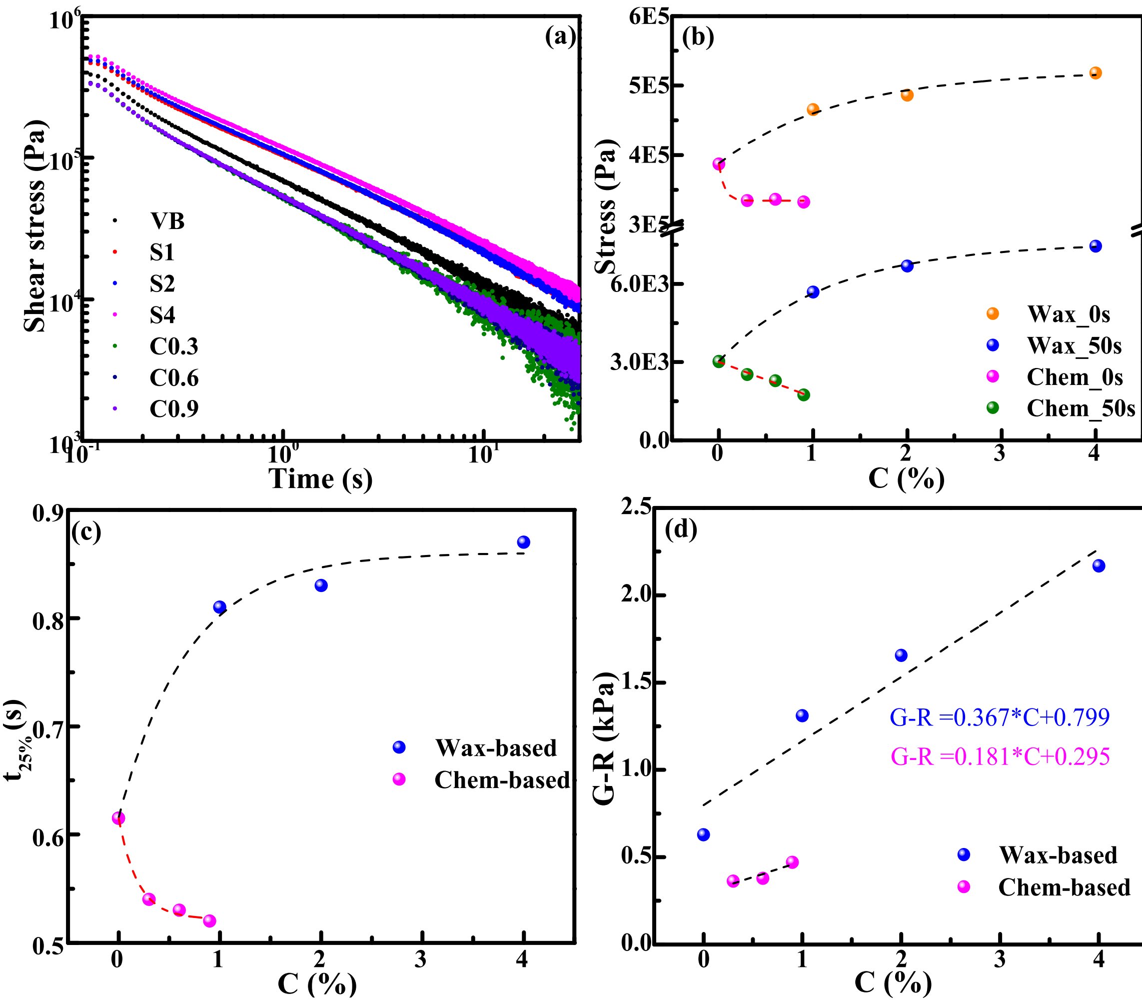

Fig. 9. Relaxation performance and G-R parameter of warm-mix bitumen.

exhibits a crystal-hardening effect, enhancing the high-temperature performance. Conversely, in heavily-aged (2 P and 4 P) bitumen, it functions as a recycling agent or softener due to lower molecular weight and chemical characteristic of saturated aliphatic hydrocarbon [21]. As a result, the wax-based WMA additive not only improves workability but also helps restore the high-temperature performance of aged bitumen to fresh bitumen level. The WMA additive reduces the RFT values for 1P- and 2P-aged PMB, while the opposite effect is observed for 4P-aged PMB. This suggests that a high level of polymer degradation amplifies the crystal-hardening effect of wax-based additive. The effect of bio-rejuvenator on RFT results are presented in Fig. 6(d). The addition of a bio-rejuvenator effectively restores the rutting performance of all warm-mix aged bitumen to fresh bitumen level. However, its impact on reducing the RFT value is less pronounced in PMB, and the rejuvenation efficiency diminished as the aging level increases. Consequently, higher quantities of bio-rejuvenator are required to treat heavily-aged (4 P) bitumen effectively.

4.4.2. Recovery percentage (R%)

Fig. 7 illustrates the $R_{0.1}$ and $R_{3.2}$ values of VB and PMB incorporating the wax-based and chemical-based WMA additives, as well as warm-mix bio-rejuvenated bitumen. The elastic recovery of all bitumen diminishes as the increase in loading stress level from 0.1kPa to 3.2kPa. Adding wax-based additive significantly enhances $R_{0.1}$ and $R_{3.2}$ values of VB and PMB, and improves their deformation resistance. The degree of improvement for PMB is notably greater than VB, possibly due to the interaction between wax-based additive and polymer network [28]. In contrast, the incorporation of the chemical-based additive leads to a slight reduction in $R_{0.1}$ and $R_{3.2}$ values. This indicates a minor weakening of high-temperature deformation resistance. For VB, the R values progressively decrease as the dosage of the chemical-based additives increases, but the reduction in R values of PMB is most pronounced at an intermediate additive dosage of 6 %. It suggests a complex interaction between the chemical-based WMA additive and the polymer matrix. While the wax-based additive significantly enhances high-temperature performance, the slight negative impact of the chemical-based additive is observed.

The higher R values of PMB than VB demonstrates its superior deformation recovery capacity due to its elastic polymer network [51]. Aging further increases the $R_{0.1}$ and $R_{3.2}$ values for both VB and PMB, attributed to the stiffness effect caused by oxidation. Notably, the R values of aged bitumen are significantly higher than warm-mix bitumen with wax-based additive, indicating that the stiffening induced by aging has a more pronounced effect on elastic recovery than the enhancement provided by wax-based additive. Interestingly, the $R_{0.1}$ value of 1PM is lower than that of the MS4 (PMB with 4 % wax-based additive), highlighting that the elastic recovery improvement of wax-based additive is more substantial than slight aging. The addition of wax-based additives consistently increases R values and enhances the high-temperature elastic recovery of all aged-VB bitumen. For PMB, the effect of wax-based additive varies with aging levels. At a slight aging level (1PM), the $R_{0.1}$ value increases after adding wax-based additive, showing enhanced elastic performance. However, at higher aging levels (2PM and 4PM), the $R_{0.1}$ value decrease, suggesting that the softening

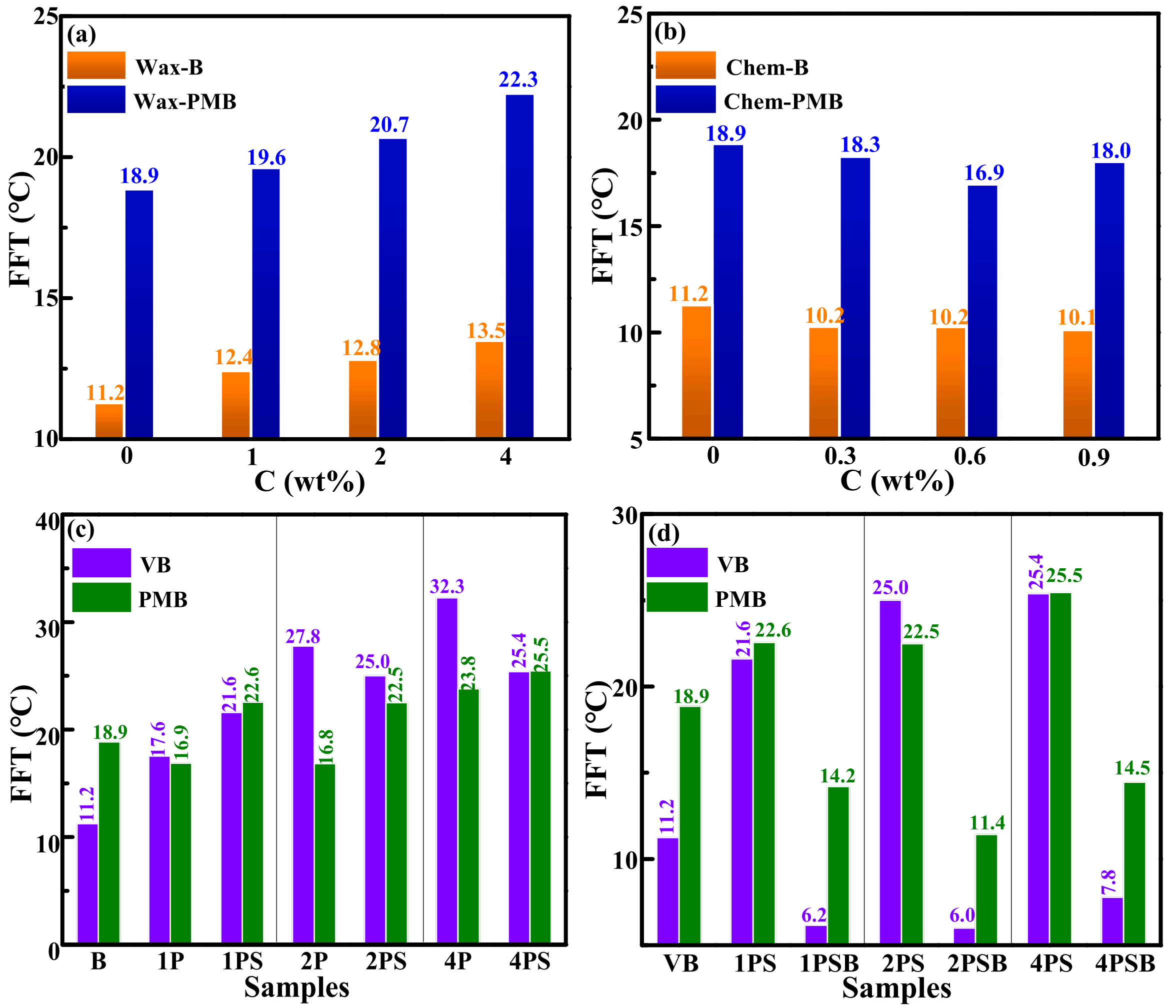

Fig. 10. Fatigue failure temperature of warm-mix bio-rejuvenated bitumen.

effect of the wax-based additive becomes dominant. Additionally, the $R_{3.2}$ values of all aged-PMB decrease after adding wax-based additives. Under high shear stress, the crystallization potential of wax-based additives is suppressed, leading to their softening effect overriding the elastic enhancement [35]. In summary, wax-based additive improves the elastic performance of aged-VB but exhibits a rejuvenating effect on heavily aged-PMB. The bio-rejuvenator further restores the $R_{0.1}$ and $R_{3.2}$ values of aged-VB and PMB toward but still higher than their fresh levels, which is more effective for aged-VB than aged-PMB.

4.4.3. Non-recoverable creep compliance (J_{nr})

The J_{nr} results are presented in Fig. 8 showing the effects of polymer, aging, WMA additive, and bio-rejuvenator on creep behavior of bitumen. The J_{nr} values of PMB are consistently lower than VB due to the positive role of polymer in improving creep resistance. For both VB and PMB, the wax-based additive reduces $J_{nr0.1}$ and $J_{nr3.2}$ values, demonstrating its effectiveness in mitigating creep deformation potential, especially for VB. Conversely, chemical-based additive increases the J_{nr} values, indicating its negative impact on creep resistance. As the chemical-based additive content increases, the J_{nr} values of VB show a steady rise, while PMB exhibits peak J_{nr} values at a dosage of 0.6 %.

The progression of aging consistently reduces the $J_{nr0.1}$ and $J_{nr3.2}$ values of VB and PMB, reflecting the stiffening effects associated with oxidation [47]. When wax-based additive is added to aged bitumen, the J_{nr} values decrease slightly. However, this reduction diminishes as aging severity increases. For PMB, the wax-based additive decreases the J_{nr} value for lightly aged-PMB (1PM) but increases the J_{nr} values for more heavily aged samples (2PM and 4PM). This suggests that wax-based additive improves deformation resistance in lightly aged-PMB but may exacerbate creep in heavily aged-PMB. For all aged bitumen, the bio-rejuvenator increases J_{nr} values, indicating partial restoration of creep compliance. Among all factors studied, long-term aging level has the most significant influence on the creep compliance of bitumen, surpassing the effects of wax-based additive and bio-rejuvenator.

4.5. Low-temperature performance

The relaxation indices, including residue stress, relaxation time corresponding to 25 % residue stress ($t_{25\ \%}$), and the G-R parameter, can effectively evaluate the low-temperature performance of warm-mix bitumen [52]. From Fig. 9, all bitumen samples exhibit a stress reduction as the relaxation time increases. However, the effect of wax-based and the chemical-based WMA additives on the relaxation curves are markedly different. The wax-based additive increases the shear stress of bitumen, attributed to the stiffness enhancement caused by crystallization at low temperatures [36]. In contrast, the chemical-based additive reduces the shear stress due to their liquid state, which lower the stiffness of the bitumen.

The shear stress of warm-mix bitumen at 0 s and 50 s is displayed in Fig. 9(b). As wax-based additive dosage increases, the shear stress rises, while increasing the chemical-based additive content results in a progressive decrease in shear stress. Notably, the impact of the chemical-based additive on shear stress is more pronounced than wax-based additive. These findings reveal the contrasting mechanisms of wax-based

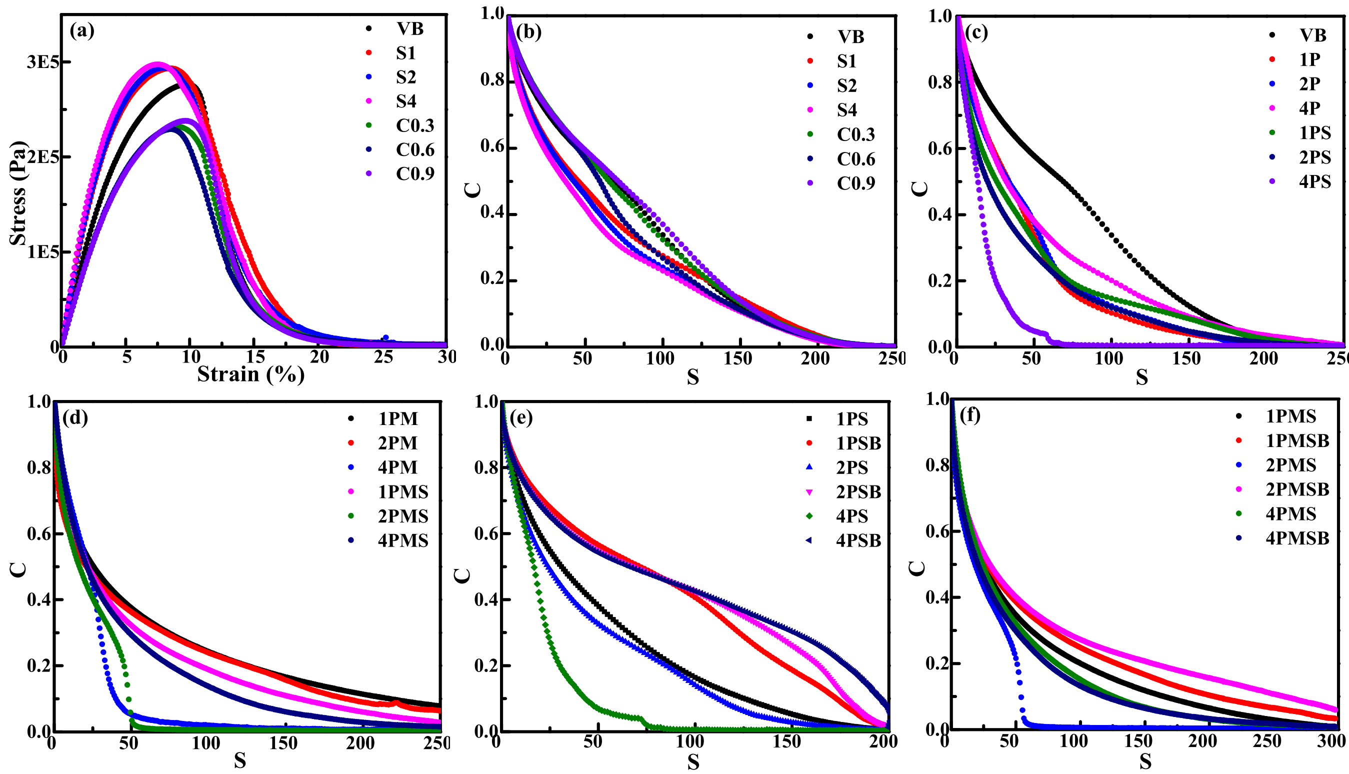

Fig. 11. Strain-stress and C-S curves of warm-mix bio-rejuvenated bitumen.

and chemical-based WMA additives on the stress relaxation behavior of bitumen. Fig. 9 (c) presents relaxation time ($t_{25\,\%}$) result, and the $t_{25\,\%}$ value of VB is approximately 0.62 s. As wax-based additive dosage increases, the $t_{25\,\%}$ value of VB continues to rise, while the chemical-based one shows an opposite effect. This means that wax-based additive deteriorates the low-temperature relaxation capacity of bitumen, while chemical-based additive enhances it. Interestingly, more WMA additives added, lower increasing rate (for wax-based additive) and decreasing rate (for chemical-based additive) in $t_{25\,\%}$ is observed. Notably, with a dosage of 1 wt%, the wax-based additive extends the $t_{25\,\%}$ by 0.19 s, whereas the chemical-based one shortens it by 0.11 s. It means that the negative impact of wax-based additive on relaxation capacity of bitumen is more significant than the positive effect of chemical-based additive.

From Fig. 9 (d), the G-R value of VB increases after adding wax-based additive and decreases with the addition of chemical-based additive, which is consistent to relaxation result. Unlike the $t_{25\,\%}$-C relationship, the G-R index increases linearly with the wax-based additive content. When more chemical-based additive is added, the G-R index tends to increase, despite the reduction in $t_{25\,\%}$ values. These discrepancies between $t_{25\,\%}$ and G-R behavior may be attributed to the differences in loading conditions between the relaxation and viscoelastic tests. However, all G-R values for bitumen with chemical-based additive remain lower than VB.

4.6. Fatigue performance

4.6.1. Fatigue failure temperature (FFT)

The fatigue failure temperature (FFT) index, defined as the temperature at which G*sinδ reaches 5000kPa, is utilized to analyse the effects of WMA additives and bio-rejuvenator on fatigue performance of VB and PMB at various aging status. The FFT results are summarized in Fig. 10, and the FFT values of PMB are higher than VB. For both VB and PMB, the addition of wax-based WMA additive increases FFT values, suggesting that wax-based additive negatively affects their fatigue resistance. After adding 4 wt% wax-based additive, the FFT value increases by 2.3°C for VB and 3.4°C for PMB, showing its more significant negative impact on PMB fatigue. It may be attributed to the reduced compatibility between the additive and the polymer components [22]. The less light fractions in PMB may facilitate easier crystallization of the wax-based additive, amplifying its adverse effect on fatigue performance. The FFT value of bitumen decreases progressively as more chemical-based additive blended, and a decreasing trend plateaus is observed as its dosage increases from 0.3 % to 0.9 %. Based on the FFT results, the optimal dosage of the chemical-based additive for PMB is determined to be 0.6 %.

The effects of aging level and the wax-based additive on FFT index are illustrated in Fig. 10(c). Initially, VB exhibits a lower FFT value than PMB, which reverses after aging and the difference becoming more pronounced as the aging level increases. It implies that PMB demonstrates better fatigue resistance than VB after aging due to its superior aging resistance. Moreover, the FFT value of VB increases gradually as the aging level rises, while the FFT value of PMB first decreases and then increases. Interestingly, the influence of the wax-based additive on FFT value depends on polymer existence and bitumen aging degree. With an aging level of 1 P, the wax-based additive increases the FFT values of aged-VB and aged-PMB, like fresh VB and PMB. Therefore, the wax-based additive deteriorates the fatigue performance of fresh and lightly aged-VB and PMB due to crystallization effect and increased stiffness.

When bitumen aging level reaches to 2 P and 4 P, the FFT values of VB decrease after adding wax-based additive, reflecting that it can improve the fatigue performance of heavily aged bitumen. This dual behavior is attributed to the two distinct functions of the wax-based additive: crystallization and softening [34]. In fresh and lightly aged bitumen, its crystallization effect mainly increases bitumen stiffness. Conversely, in heavily aged bitumen, its softening effect becomes more prominent, reducing stiffness and enhancing fatigue resistance. For PMB, adding wax-based additive increases FFT value and negatively affects fatigue resistance at all aging status. At the 4 P aging level, the FFT value of PMB increases from 23.8°C to 25.5°C, after adding the

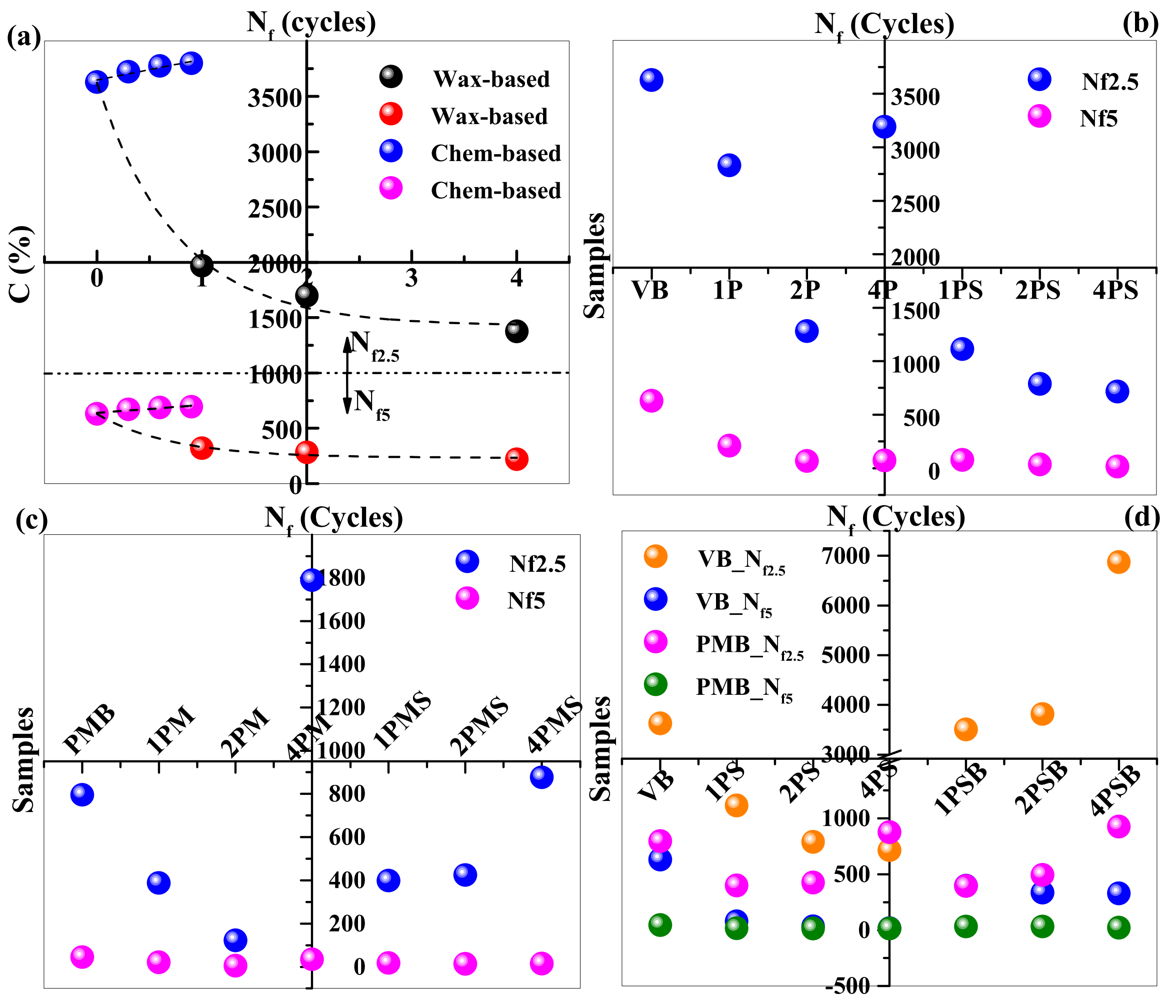

Fig. 12. Fatigue life of warm-mix rejuvenated bitumen at both 2.5 % and 5.0 % strain levels.

wax-based additive. It suggests that the negative effect of wax-based additive on fatigue resistance of PMB becomes less pronounced as aging level increasing.

Fig. 10(d) illustrates the FFT values of warm-mix aged-VB and aged-PMB during bio-rejuvenation process. Regardless of aging level, adding bio-oil effectively enhances the fatigue resistance of aged-VB and aged-PMB with wax-based additive. Notably, the FFT values of all bio-rejuvenated bitumen are lower than VB, suggesting that bio-oil fully restores the fatigue performance of aged-VB. Furthermore, the rejuvenation effect of bio-rejuvenator on FFT is more pronounced for VB than PMB. As a result, VB exhibits lower FFT values than PMB after adding bio-rejuvenator, even when the FFT value of 2 P aged-VB is higher than aged-PMB. The combination of the wax-based additive and bio-rejuvenator can achieve dual objectives of facilitating warm-mix and rejuvenating aged bitumen, especially enhancing fatigue resistance.

4.6.2. *Fatigue damage behavior*

The strain-stress and material integrity-damage (C-S) curves of warm-mix bitumen are plotted in Fig. 11. The addition of the wax-based additive results in an increase in maximum stress and a rightward shift of the maximum strain of VB, indicating enhanced rigidity and stress-bearing capacity. In contrast, the chemical-based additive reduces maximum stress, reflecting a softening effect. As the dosage of the wax-based additive increases, the maximum stress continues to rise, while the corresponding strain decreases. The material integrity of bitumen declines as the wax-based additive content increasing, which accelerates bitumen degradation during fatigue loading. Conversely, the chemical-based additive demonstrates an enhancement in material integrity and improves fatigue resistance of bitumen, which aligns with the softening effect of the chemical-based additive.

Fig. 11(c) and (d) illustrate the fatigue damage behavior of the warm-mix aged-VB and aged-PMB, and high aging degree significantly accelerates fatigue damage due to reduced relaxation capacity and increased brittleness. The wax-based additive weakens the material integrity of aged-VB, especially for aging level of 4 P. For PMB, it lowers fatigue resistance of 1PM and 2PM, but enhances that of 4 PM, likely due to improved interaction between degraded polymer chains [28]. Fig. 11 (e) and (f) show that bio-oil effectively restores C-S curves on aged-VB and PMB. This improvement is likely due to the bio-oil's ability to restore flexibility and reduce brittleness by rebalancing chemical composition and mitigating aging effect. However, the rejuvenation effect of bio-oil is limited in 4 P aged-PMB, suggesting that the advanced degradation of polymer chains in this state diminishes the rejuvenation efficiency of the bio-oil.

4.6.3. *Fatigue life (N_f)*

The fatigue life results of warm-mix rejuvenated bitumen under strain-controlled conditions at 2.5 % and 5.0 % strain levels are presented in Fig. 12. Fatigue life (N_f) is a key parameter for evaluating the bitumen durability. Increasing the strain level significantly reduces fatigue life ($N_{f5} < N_{f2.5}$), with this effect being particularly pronounced for VB. Fig. 12(a) reveals contrasting impacts of wax-based and chemical-based additives on fatigue life. Wax-based additive decreases $N_{f2.5}$ and N_{f5} of VB, following a logarithmic downward trend with increasing

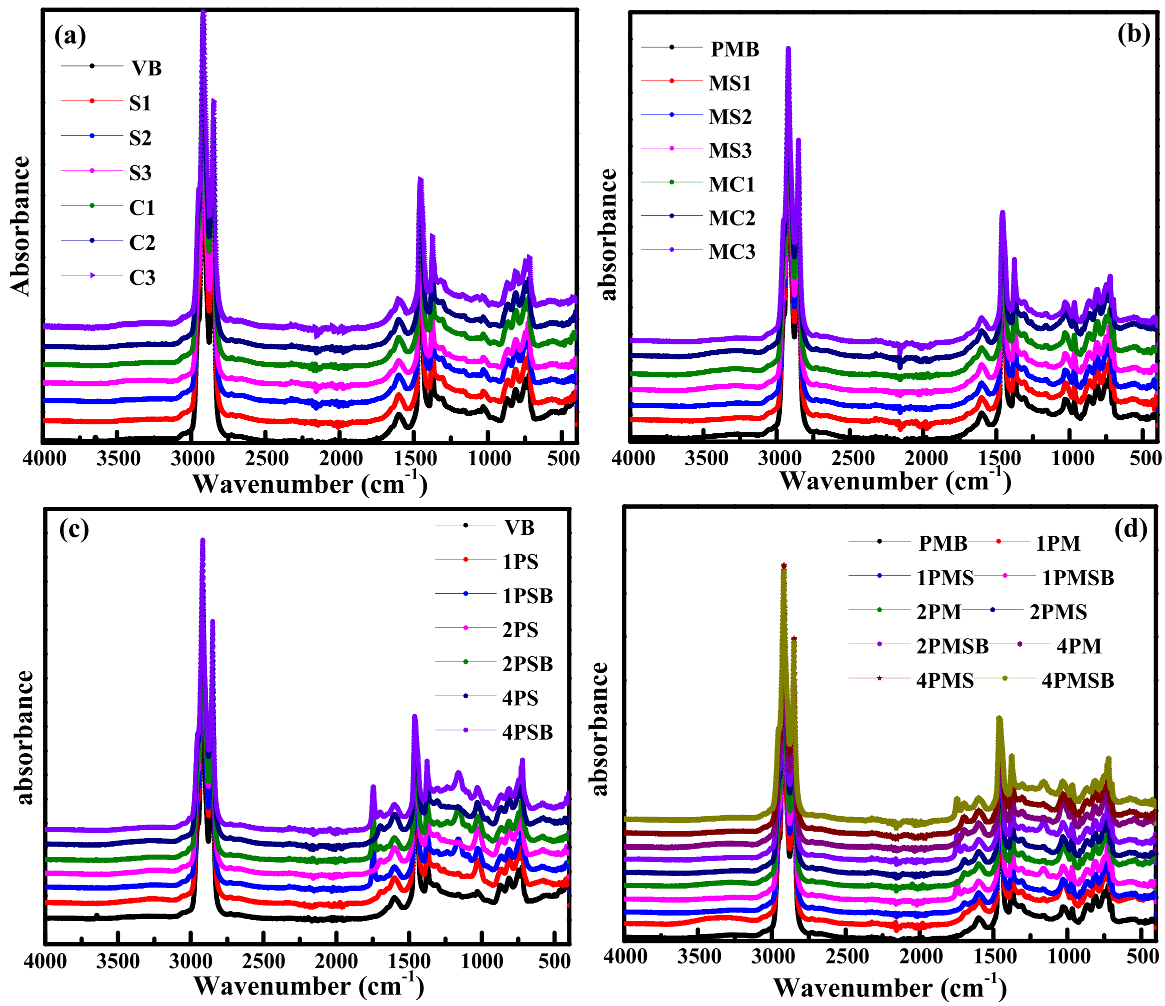

Fig. 13. FTIR curves of warm-mix bio-rejuvenated bitumen.

dosage. Conversely, chemical-based additive linearly increases $N_{f2.5}$ and N_{f5} versus dosage. It shows that wax-based additive impairs fatigue resistance, while chemical-based additive enhances it. Long-term aging reduces $N_{f2.5}$ and N_{f5} of bitumen, and PMB exhibits a slower reduction in fatigue life than VB due to the anti-aging capacity conferred by the polymer network. The wax-based additive further decreases fatigue life of aged-VB, particularly for $N_{f2.5}$, indicating that wax-based additive exacerbates the reduction in fatigue resistance caused by aging. However, wax-based additive significantly increases $N_{f2.5}$ of 1PM and 2PM, indicating that it can extend the fatigue life of aged-PMB with low aging levels.

Fig. 12(d) displays fatigue life of warm-mix bio-rejuvenated bitumen. The incorporation of bio-rejuvenator improves $N_{f2.5}$ and N_{f5} of aged bitumen with wax-based additive, especially for aged-VB. This indicates that bio-oil effectively restores the fatigue performance of aged-VB, counteracting the negative effect from wax-based additive. The $N_{f2.5}$ values of several warm-mix bio-rejuvenated bitumen exceed fresh VB, showing the bio-rejuvenator's remarkable efficacy. However, the effect of bio-oil on improving the fatigue life of aged-PMB is limited.

4.7. Chemical properties

The FTIR curves of warm-mix bio-rejuvenated bitumen and PMB are plotted in Fig. 13(a) and (b), respectively. There is no new peak observed after adding the wax-based and chemical-based additives, indicating that the main modification mechanism between both WMA additives with VB and PMB is physical interaction without any chemical reaction. Additionally, the FTIR curves of aged bitumen with the wax-based additive and bio-rejuvenators are shown in Fig. 13(c) and (d). The long-term aging results in the increase in carbonyl peak at 1700 cm^{-1} and sulfoxide peak at 1030 cm^{-1} of virgin and polymer modified bitumen. Meanwhile, the addition of the wax-based additive has no effect on the functional group types of aged bitumen. After adding the bio-oil, two new peaks at around 1720 cm^{-1} and 1110 cm^{-1} occur, which is related to the ester group (-O-C═O) present in the bio-oil [53].

Fig. 14 presents the chemical indices of all warm-mix bitumen. The aromaticity index of VB and PMB decreases as WMA additive content increases, reflecting a reduction in aromatic fractions. For VB, the decline trend is more gradual after adding wax-based additive than adding chemical-based additive. In contrast, PMB exhibits a distinct and linear decrease in aromaticity index after adding WMA additives, and the chemical-based additive showing a particularly pronounced effect. This suggests that the chemical-based additive has a strong dilutive impact on the aromatic molecular structures in both VB and PMB [12]. Notably, the reduction in aromaticity index of PMB due to the wax-based additive is more significant than VB, associated with a greater interaction between the polymer network and the wax-based additive [6]. A reduction in aromaticity, particularly with chemical-based WMA additive, decreases polycyclic aromatic compounds in bitumen, altering its properties. In PMB, this affects polymer compatibility, potential leading to phase separation or changes in viscoelastic behavior.

The aliphatic index shown in Fig. 14(b) rises as wax-based additive dosage increases, indicating an enrichment of aliphatic structures contributed by the wax-based additive. The increase is more distinct for

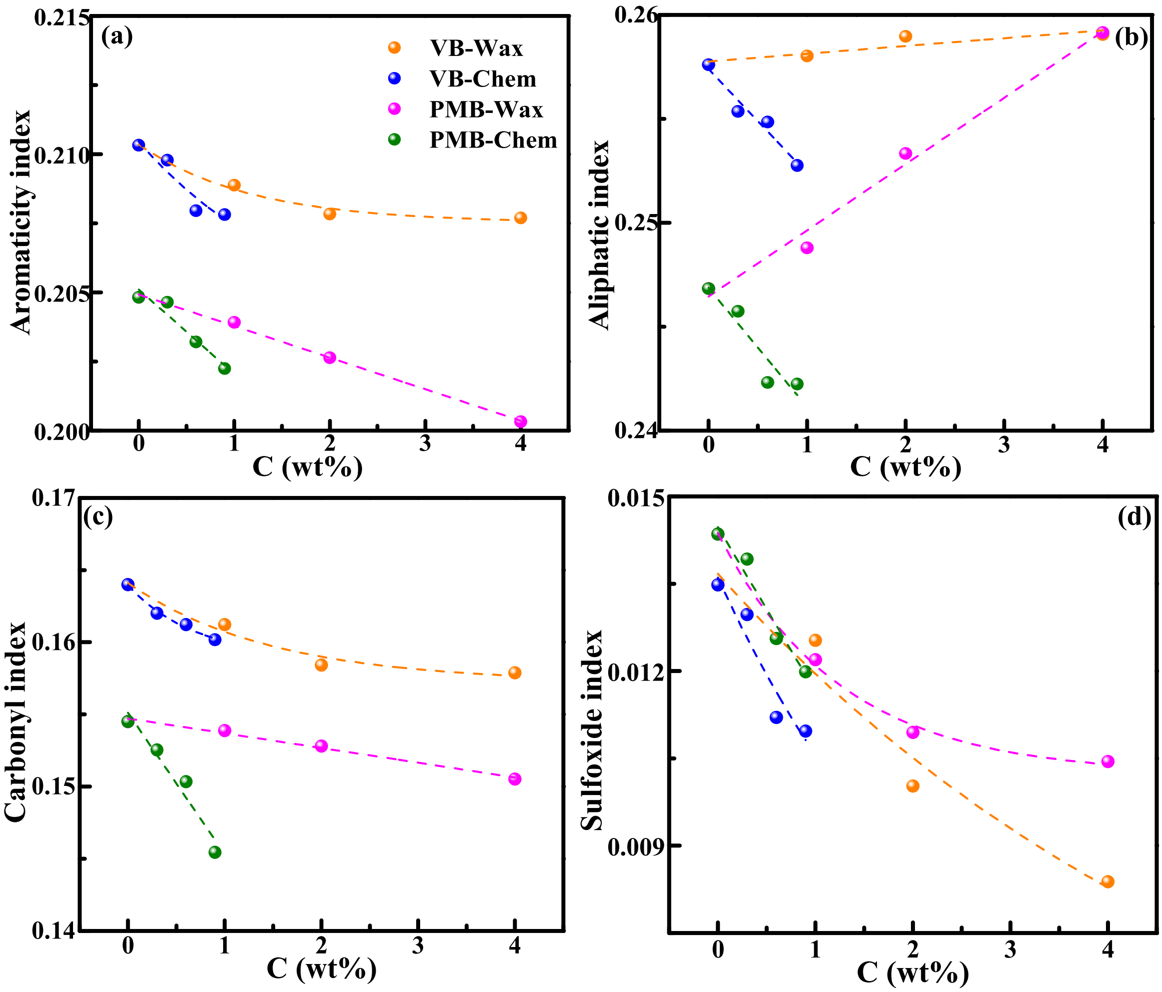

Fig. 14. Chemical performance of warm-mix VB and PMB.

PMB than for VB, likely due to stronger interactions between the polymer matrix and wax-based additive [28]. An increase in aliphatic, as observed with wax-based WMA additive, shifts bitumen composition toward long-chain hydrocarbons. In PMB, this enhances structural integrity, increasing stiffness and rutting resistance but potentially reducing fatigue life [21]. Higher aliphatic content also improves oxidation resistance, as aliphatic compounds are less reactive to oxygen, while enhancing moisture resistance, thereby reducing stripping risks in asphalt pavements [6]. In contrast, the aliphatic index of VB and PMB decreases linearly after adding more chemical-based additive with similar decreasing rate. In summary, wax-based additive enriches aliphatic content and reduces aromaticity of bitumen, while the chemical-based additive uniformly dilutes both aromatic and aliphatic groups.

Fig. 14(c) and (d) shows the carbonyl (C=O) and sulfoxide (S=O) index, critical markers of oxidative aging in bitumen [54]. For both VB and PMB, the carbonyl index decreases with increasing additive dosage. This reduction effect of chemical-based additive is more significant than wax-based additive, indicating that chemical-based additive has a stronger dilutive effect on the C=O groups in bitumen. Moreover, the chemical-based additive exhibits a greater impact on reducing the C=O index in PMB than in VB. The interaction between the chemical-based

Table 5
Pearson correlation coefficient values between chemo-rheological properties.

	η_0	RFT	G*	δ	$R_{0.1}$	$J_{nr0.1}$	$R_{3.2}$	$J_{nr3.2}$	FFT	$N_{f2.5}$	N_{f5}
AI	0.192	0.241	0.004	0.382	0.448	0.422	0.377	0.400	0.072	0.124	0.382
AII	<u>0.692</u>	0.342	0.384	0.330	0.261	0.061	0.261	0.052	0.109	0.092	0.139
CI	0.183	0.564	0.333	<u>0.705</u>	<u>0.711</u>	<u>0.693</u>	<u>0.667</u>	<u>0.671</u>	0.221	0.347	<u>0.711</u>
SI	0.023	0.034	0.187	0.052	0.173	0.076	0.076	0.043	0.223	0.428	0.306
RFT	0.670										
G*	0.587	***0.849***									
δ	0.635	***0.971***	0.794								
$R_{0.1}$	0.539	***0.927***	0.716	***0.953***							
$J_{nr0.1}$	0.358	0.778	0.520	0.789	***0.829***						
$R_{3.2}$	0.575	***0.965***	0.762	***0.975***	***0.976***	0.798					
$J_{nr3.2}$	0.362	0.801	0.545	0.802	0.835	***0.995***	0.822				
FFT	0.255	0.683	***0.827***	0.585	0.582	0.585	0.632	0.625			
$N_{f2.5}$	0.018	0.472	0.527	0.422	0.483	0.522	0.464	0.535	0.704		
N_{f5}	0.349	0.816	0.650	0.831	0.886	***0.932***	0.844	***0.936***	0.687	0.762	

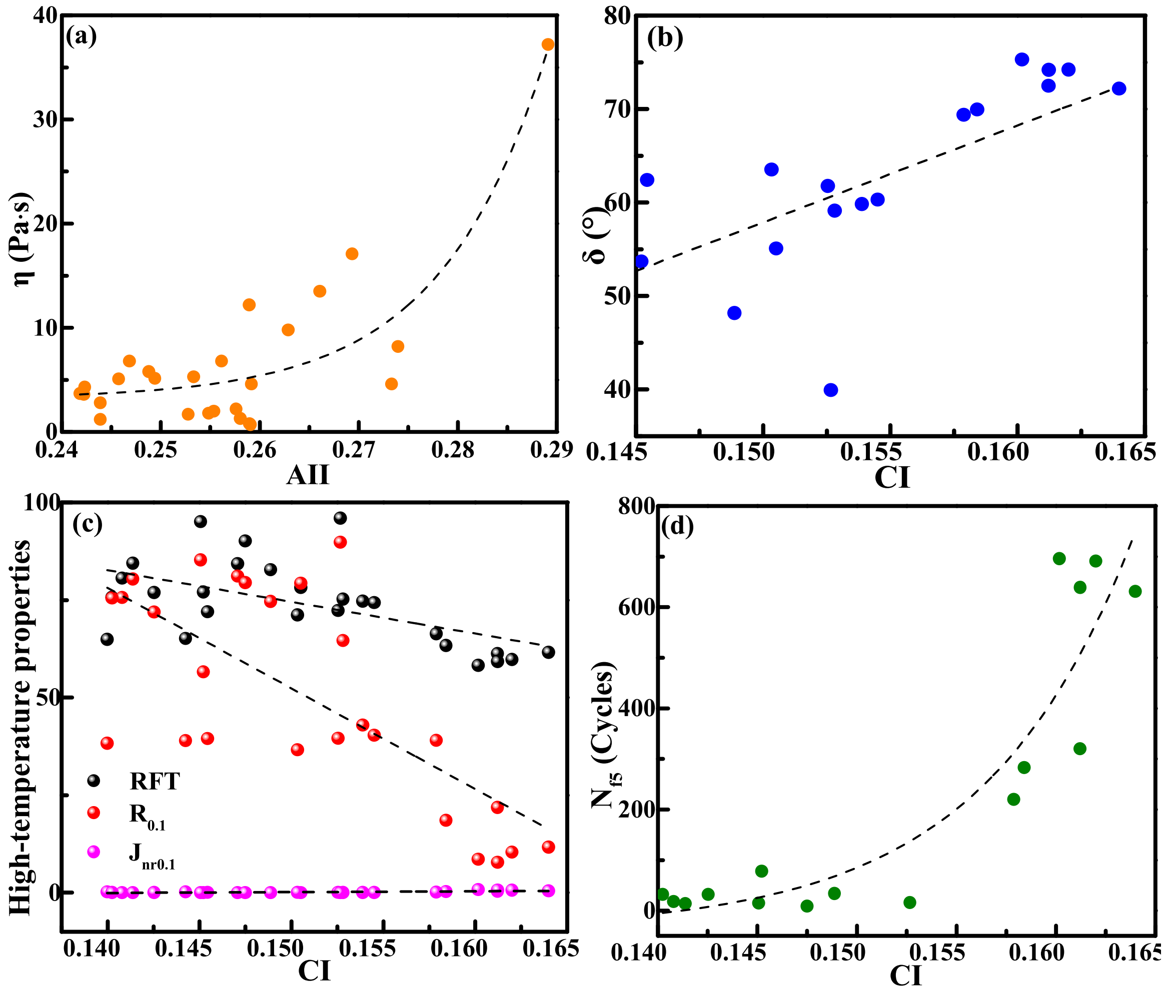

Fig. 15. Chemo-rheological correlations of warm-mix bio-rejuvenated bitumen.

additive and the polymer matrix in PMB enhances the dilution of oxidative aging products [33]. Additionally, both WMA additives reduce the sulfoxide index, and chemical-based additive demonstrates a more significant effect than wax-based additive. Interestingly, the wax-based additive reduces more S=O in VB than in PMB, because VB has a more homogeneous structure, making it easier for the wax-based WMA to influence oxidation [36]. In contrast, the polymer network in PMB restricts the impact of the wax-based WMA but allows chemical-based additive to interact more effectively.

4.8. Chemo-mechanical correlation of warm-mix bio-rejuvenated bitumen

Investigating the chemometric correlations of warm-mix bio-rejuvenated bitumen is essential for optimizing the performance of WMA additives and bio-oils. This study utilizes Pearson correlation analysis to explore relationships between rheological properties (η_0, RFT, G*, δ, $R_{0.1}$, $J_{nr0.1}$, $R_{3.2}$, $J_{nr3.2}$, FFT, $N_{f2.5}$, and N_{f5}) and chemical indices (AI, AII, CI, and SI). Table 5 summarizes the Pearson correlation coefficients with values exceeding 0.650 highlighted for emphasis. Notably, the aromatic index (AI) and sulfoxide index (SI) show weak correlations with all rheological indicator, while the aliphatic index (AII) correlates strongly with zero-shear viscosity (η_0). The carbonyl index (CI) exhibits significant correlations with multiple rheological parameters, including δ, $R_{0.1}$, $J_{nr0.1}$, $R_{3.2}$, $J_{nr3.2}$, and N_{f5}.

Fig. 15(a) reveals a strong non-linear relationship between AII and η_0, where increasing AII is associated with a sharp rise in zero-shear viscosity. This trend suggests that higher AII enhances stiffness and molecular cohesion within the bio-rejuvenated bitumen. In Fig. 15(b), the linear relationship between CI and phase angle indicates that increasing CI promotes a more elastic bitumen response, reflective of improved viscoelastic behavior. Fig. 15(c) and (d) further examine the correlations between CI and high-temperature properties and fatigue performance. As CI increases, RFT and $R_{0.1}$ value decline, indicating a slight reduction in rutting resistance, while $J_{nr0.1}$ increases slightly. Notably, the fatigue life (N_f) demonstrates an exponential increase with CI, signifying improved fatigue resistance, likely due to enhanced chemical restoration and better dispersion of WMA additive and bio-oil within the bitumen.

5. Conclusions and recommendation

This study examines the combined impact of warm mix asphalt (WMA) additives and bio-oil on virgin bitumen (VB) and polymer-modified bitumen (PMB) with different aging degrees. Notably, the dual benefits of warm-mix bio-rejuvenators—improving both stiffness and fatigue resistance—underscore the importance of balancing rutting resistance with long-term durability to achieve optimal bitumen performance. The key findings are summarized below:

(1) The viscosity of VB increases significantly after long-term aging 80 h, while PMB exhibits a comparatively smaller increase from 6.8 Pa˙s to 16.2 Pa˙s, indicating its superior resistance to aging. Wax-based WMA additive reduces viscosity of VB more effectively, following an exponential decline, while chemical-based

one exhibits a linear decrease and is more effective for PMB. Wax-based additive achieves only a 9.1 % viscosity reduction of aged-VB, whereas bio-oil consistently provides a greater percentage reduction.

(2) The wax-based additive enhances the high-temperature rutting resistance, whereas the addition of 0.9 wt% chemical-based additive reduces the rutting failure temperature (RFT) by 3.3°C for VB and 2.3°C for PMB. Wax-based additive acting as rejuvenator in heavily aged bitumen. Wax-based additive improves elastic recovery, particularly in PMB, while chemical-based one shows negative effect. Bio-oil rejuvenator restores elasticity, though higher dosages are needed.

(3) Wax-based additive increases shear stress and G-R index due to crystallization, while chemical-based one enhances relaxation capacity of aged bitumen. The addition of the wax-based additive reduces fatigue resistance, as indicated by an increase in the fatigue failure temperature (FFT) of 2.3°C for VB and 3.4°C for PMB upon incorporating 4 wt% of the WMA additive. The chemical-based additive and bio-rejuvenator show positive impact on extending fatigue life of aged VB. Based on the FFT results, the optimal dosage of the chemical-based additive for PMB is determined to be 0.6 %.

(4) Both WMA additives modify bitumen primarily through physical interaction rather than chemical reactions. The chemical-based additive significantly reduces aromaticity, particularly in PMB, whereas the wax-based additive increases the aliphatic content. Strong chemo-mechanical correlations indicate that wax-based bio-rejuvenated bitumen, characterized by higher AII and CI indices, exhibits superior rutting resistance and expanded fatigue life.

This study offers limited insight into the mechanisms driving the varied effects of WMA additives and aging on the chemo-rheological properties of bio-rejuvenated bitumen. Future research should employ advanced methods, such as molecular dynamics (MD) simulations, to explore interactions between WMA additives, bio-oils, and PMB at the molecular level under aging conditions. To better evaluate real-world performance, material characterization should also extend to the mastic, mortar, and mixture scales, and long-term aging resistance and thermal stability of warm-mix rejuvenated bitumen will be studied. To enhance practical applicability of the proposed WMA additives, further studies are recommendations to explore its performance within drying mixing processes. Moreover, in-depth investigation into long-term durability, particularly aging and moisture susceptibility, is vital for developing durable and resilient asphalt pavement in diverse environmental and loading conditions.

CRediT authorship contribution statement

Ahmed Majeed: Investigation, Formal analysis, Data curation. **Shisong Ren:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Aikaterini Varveri:** Writing – review & editing, Supervision, Resources, Methodology, Investigation. **Wim Van den bergh:** Writing – review & editing, Supervision, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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