Construction and Building Materials 438 (2024) 137268

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Recovering the properties of aged bitumen using bio-rejuvenators derived from municipal wastes

Yongping Hu [a,*], Eman Omairey [b], David Hughes [b], Helen Bailey [c], Miles Watkins [d], John Twitchen [d], Gordon D. Airey [a], Anand Sreeram [a,*]

[a] Nottingham Transportation Engineering Centre (NTEC), Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK
[b] School of Computing, Engineering and Digital Technologies, Teesside University, Middlesbrough TS1 3BA, UK
[c] The Driven Company Associates Limited, Beverley HU17 8HL, UK
[d] Stuff4Life, Redcar TS10 4RF, UK

ARTICLE INFO

Keywords:
Bitumen
Rejuvenation
Rheology
Black space
Bio-binder
Thermal stability

ABSTRACT

Ageing of bitumen leads to significant performance deterioration of asphalt pavements and leads to material properties that are not conducive to recycling. Aiming to maximise the reusability of bitumen, this study investigated the feasibility of rejuvenating aged bitumen using bio-based rejuvenators synthesised from municipal wastes. Two bio-rejuvenators were used in this study, namely Rej-A which was a crude polymer with bio-waste pyrolysis dense fractions and Rej-B which was a filtered pyrolysis wax further derived from Rej-A. The bio-rejuvenators, virgin, aged, and rejuvenated bitumen were characterised using a comprehensive testing programme of gas chromatography and mass spectrometry (GC-MS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), multiple stress creep and recovery (MSCR), linear amplitude sweep (LAS), and frequency sweep tests. It was observed that both bio-rejuvenators produced in this study can effectively recover the rheological properties of aged bitumen, improving its fatigue performance, e.g. the fatigue lives (at 15 % strain level) of Rej-A and Rej-B rejuvenated bitumen were 5.4 times and 3.0 times of that for aged bitumen when the dosage was 14 %. The rejuvenated bitumen was more sensitive to strain while less sensitive to temperature compared with virgin bitumen. Overall, Rej-A outperformed Rej-B in recovering the properties of aged bitumen. However, Rej-A was thermally unstable, undergoing 15.6 % mass loss when heated to 160 °C.

1. Introduction

Roads are one of the most important infrastructure assets of transportation networks. The design life of roads is limited by the deterioration in the performance of the binding material, termed as bitumen, especially related to ageing [1,2]. Serious distresses of asphalt pavements are induced due to the ageing of bitumen, such as cracking, potholes, stripping, etc, which negatively affect the usability of pavements [3–5]. Ageing changes the chemical composition of bitumen through oxidisation and steric hardening processes [5,6]. Consequently, the mechanical properties of bitumen deteriorate, leading to eventual damage and failure. The chemical reaction between atmospheric oxygen and bitumen, termed as oxidisation, is the primary attribute of ageing. This reaction results in major chemical changes such as large differences in the ratio between molecule sizes and the ratio of polar and non-polar compounds which reduces ductility and consequently diminishes bitumen performance [7]. Steric hardening is the hardening of bitumen over time at room temperature. It occurs after bitumen is melted, which leads to formation of ordered structures within bitumen such as asphaltenes [8,9].

Ageing leads to better resistance to rutting while the resistance to fatigue and thermal cracking of bitumen is reduced [10]. Chemically, ageing of bitumen contributes to the reduction in the content of aromatics and the increase of asphaltenes, inducing instability of its colloidal system [11]. The carbonyl and sulfoxide chemical functional groups can be regarded as fingerprints of ageing and show an increasing trend with time [12,13]. Molecularly, ageing leads to increased molecular weight within bitumen and leads to the increase of viscosity [14]. Thermally, the glass transition temperature increases after ageing, caused by the increase of the content of asphaltenes [15]. It can be

* Corresponding authors.
E-mail addresses: yongping.hu@nottingham.ac.uk (Y. Hu), anand.sreeram@nottingham.ac.uk (A. Sreeram).

https://doi.org/10.1016/j.conbuildmat.2024.137268
Received 10 February 2024; Received in revised form 30 May 2024; Accepted 26 June 2024
Available online 28 June 2024

concluded that ageing of bitumen is an intricate phenomenon which ultimately results in the performance deterioration of asphalt pavements.

The reuse of bitumen in the form of recycled asphalt pavement (RAP) materials in new pavement construction applications has been widely promoted as it increases the circularity of the materials used and reduces overall carbon emissions [16–18]. However, reusing of aged bitumen in RAP is difficult as it is more susceptible to thermal and fatigue cracking. The introduction of rejuvenators provides a practical solution to reuse aged bitumen, as rejuvenators have the capacity to recover some of its desired properties [19]. Previous studies revealed that the rejuvenation mechanisms can be attributed to breaking down of asphaltene microstructures into smaller sizes, facilitating the diffusion of aged and virgin binders, as well as diluting the mix to increase diffusion rate [20–22]. Rejuvenators are defined as chemical additives which can be used to recover the physical properties of aged bitumen, such as reducing its viscosity and improving its cracking resistance ability by restoring the viscoelastic balance. There are several rejuvenators available in the market such as petroleum-based and bio-based commercial oils, tall oils, waste kitchen oils, waste industrial oils etc. Out of these, bio rejuvenators produced from biobased materials have recently become popular due to its promising rejuvenation efficiency and the overall industry focus on sustainability [23,24]. Bio-rejuvenators can be produced through recycling of wastes, such as waste cooking oils and municipal wastes, which makes it an environmentally friendly option compared to other types of rejuvenators.

Previous studies in this area have suggested that the organic fractions of municipal wastes, produced after thermochemical treatments could potentially be used as bio-rejuvenators to recover the deteriorated performance of aged bitumen [25,26]. Municipal waste comprises a composite blend primarily consisting of biomaterials and plastics. Processing these materials in their composite state holds promise as a pragmatic solution as use of composite rejuvenators is encouraged to diversify the softening and restoration processes in bitumen [27]. There are several methods to breakdown municipal wastes to obtain desirable properties, such as pyrolysis, gasification, and anaerobic digestion. Pyrolysis is the most widely used method and is defined as the thermochemical decomposition of organic material that occurs at temperatures of 300–500 °C in the absence of oxygen [28]. These produced biomaterials such as bio-rejuvenators, biochar etc. have shown to have potential for direct application in bitumen recycling and modification [29–31]. For example, biochar can be used to modify bitumen to reduce rate of ageing, or improve ageing resistance [29]. Similarly, the use of bio-rejuvenators could increase the colloidal stability of aged bitumen and deagglomerate asphaltenes [30].

Despite these promising studies, a comprehensive understanding of the use of organic fractions of municipal wastes to recycle aged bitumen is limited. Previous studies have only investigated some fundamental properties of such bio-rejuvenators rejuvenated bitumen, such as modulus and viscosity [25]. The comprehensive characterisation and mechanism analysis of the rejuvenation process is unclear, which limits the large-scale application of municipal wastes derived bio-rejuvenators. In view of that, this study used two municipal wastes derived bio-rejuvenators and evaluated their ability to restore the properties of aged bitumen. It is envisaged that comprehensive performance evaluation of bitumen rejuvenated by these bio-rejuvenators can potentially provide an effective value-added approach to reuse waste materials while reducing the need for other disposal methods.

2. Scope

This study aims to comprehensively evaluate the feasibility of using municipal wastes derived bio-rejuvenators to restore the properties of aged bitumen. Firstly, two bio-rejuvenators were produced from municipal wastes using pyrolysis treatment. Following this, aged bitumen was rejuvenated using the synthesised bio-rejuvenators at various percentages. Comprehensive tests such as multiple stress creep and recovery (MSCR) tests, linear amplitude sweep (LAS) tests, frequency sweep tests were then carried out to investigate the rheological properties of the rejuvenated bitumen. Overall, this work systematically evaluated the feasibility of using municipal wastes derived bio-rejuvenators as effective recycling-based additives for aged bitumen.

3. Materials and methods

3.1. Materials

The bitumen used in this study was an unmodified 70/100 penetration grade bitumen, the physical and chemical properties of bitumen are listed in Table 1. The SARA fractions i.e. the component content of saturates, aromatics, resins and asphaltenes in the bitumen is also illustrated.

Two rejuvenators derived from municipal wastes were used in this study. Specifically, a mixture of crude polymer and bio-waste pyrolysis dense fractions (labelled as Rej-A), and a mixture of filtered polymer and bio-waste pyrolysis wax (labelled as Rej-B). The municipal waste feedstock consisted of 30 % mixed waste plastic (consisting mainly of high-density polyethene (> 90 %) with other waste plastics) and 70 % bio-wastes (crude sewage sludge and agricultural wastes). Pyrolysis was carried out at a heating rate of 16 °C/min with a residence time of 15 minutes using a stainless-steel tube furnace under a controlled nitrogen environment (flow rate of 1.5 L/min) at 600 °C and the dense fractions were condensed in a catch pot from the nitrogen purge. The pyrolysis programme was selected to optimise the production of wax and oil products from specified feedstock, following a series of trials aimed at maximising content yield. The pyrolysis plant, manufactured by Pyrolyze, is shown in Fig. 1.

The curd pyrolyzed dense fraction produced from the pyrolysis process was named Rejuvenator A (Rej-A). It emitted a pungent odour and consisted of a wax, bio-oil, and char mixture. Rejuvenator B (Rej-B) was further refined to remove light fractions and chars using fractional crystallisation. Initially, the raw mixture was heated to melt waxes, after which solid impurities were filtered out, leaving behind a mixture of waxy and liquid substances. This mixture was then cooled to allow the waxy fractions to crystallise, which were subsequently separated from any remaining moisture and low molecular weight liquids. As a result, this process yielded a uniform waxy material with consistent colour and texture. The basic properties of these bio-rejuvenators are listed in Table 2.

3.2. Characterisation methods

3.2.1. Ageing and rejuvenation of bitumen

The virgin bitumen was aged using a rolling thin film oven (RTFO) at 163 °C for 75 mins as per BS EN 12607–1 [32]. The residue was then subjected to pressure ageing vessel (PAV) ageing at 100 °C and 2.1 MPa as per BS EN 14769 [33] with extended duration period of 40 hours. After ageing, the bitumen was rejuvenated using the synthesised bio-rejuvenators. During the rejuvenation process, the aged bitumen was heated to 160 °C then weighed accurately. Afterwards, the rejuvenators were introduced to the aged binders at dosages of 6 %, 10 %, 14 % and 18 %, respectively and blended for around 15 minutes. These specific dosages were selected based on preliminary tests and previous reported studies [34,35].

3.2.2. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

TGA and DSC were carried out using PerkinElmer Simultaneous Thermal Analyser STA 6000. The purge gas used was argon. This technique allowed to evaluate material mass change as well as its heat flow as a function of temperature and time. It also enabled identification of endothermic and exothermic processes (e.g., melting and

Table 1
Basic properties of bitumen used in this study.

Property	Penetration (0.1 mm)	Softening point (°C)	PG	Viscosity at 135 °C (mPa·s)	SARA
Value	81	45.5	PG 70–22	306	4.4:58.9:20.6:16.1

Fig. 1. Pyrolysis unit for production of rejuvenators.

Table 2
Basic properties of bio-rejuvenators.

Label	Phase at 25 °C	Viscosity at 60 °C (mPa·s)	Components	Appearance
Rej-A	Gel	6	wax, bio-oil and char	
Rej-B	Solid	623	waxy compounds of Rej-A	

crystallisation) to characterise the thermal response of materials [36–40]. The temperature was set to gradually increase from 30 to 250 °C at a rate of 10 °C/min, then gradually cooled down from 250 to 30 °C at a rate of 50 °C/min, maintaining the temperature at 30 °C for 15 minutes. This cycle was repeated twice to observe changes in the thermal behaviour after one heating/cooling cycle and any mass losses upon reheating.

3.2.3. Gas Chromatography-flame ionisation detection (GC-FID) and mass spectrometry (MS)

GC-MS analysis was carried out to determine the fatty acid content within their soluble phase (after filtering out any char or biochar from the specimens). The procedure followed to determine the fatty acids content was based on established literature in the area [41,42]. Additionally, due to the presence of volatile components in these crude pyrolysis products, GC-FID analysis was first carried out to analyse and separate volatile mixtures.

3.2.4. Frequency sweep tests on bitumen using a dynamic shear rheometer (DSR)

The frequency sweep tests were conducted at a constant strain level of 0.2 % to ensure the linear viscoelastic (LVE) response of the bitumen. The tests were carried out over the temperature range of 10–70 °C at an interval of 10 °C and frequencies ranging from 0.1 rad/s to 100 rad/s (0.0159 Hz-15.9 Hz) with ten readings per decade. The test geometry configuration consisted of 25 mm parallel plates with a gap of 1 mm.

3.2.5. Linear amplitude sweep test on bitumen using a DSR

The linear amplitude sweep (LAS) test included frequency sweep and linear amplitude sweep procedures. Firstly, a frequency sweep test at 0.1 % strain over a range of frequencies from 0.2 to 30 Hz was performed. Subsequently a "stepped" linear amplitude sweep test consisting of 10-second intervals of constant strain amplitude was employed, with each interval followed by another interval of increased strain amplitude as follows: 0.1 %, 1–30 % with an increase of 1 % strain per ramp as per AASHTO T391–20 [43]. The temperature used for the LAS tests were 25 °C.

3.2.6. Multiple stress creep and recovery test on bitumen using a DSR

The Multiple Stress Creep and Recovery (MSCR) test was conducted at 70 °C with a configuration of 25 mm parallel plates and 1 mm gap as per BS EN 16659:2015 [44]. The specimen was loaded at a constant creep stress of 0.1 kPa for 1 second duration followed by a zero-stress recovery period of 9 seconds duration. The procedure was repeated for 10 cycles without any rest periods. The creep-recovery sequence was then repeated for another 10 cycles at a load of 3.2 kPa without rest periods.

3.2.7. Attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy

A spectrometer equipped with an attenuated total reflection (ATR) unit was employed in this study. The scanning range of the spectra was 4000–600 cm^{-1} with the resolution of 4 cm^{-1} and 24 scans. Before the formal scanning of the bitumen samples, the background scanning was performed. To avoid the change of baseline, once the background was recorded, the samples were loaded onto the crystal within one minute [45]. Each specimen was scanned with three replicates. After the measurement, a suitable, nontoxic bitumen solvent (white spirit) was used to clean the diamond crystal.

4. Results and discussion

4.1. Physiochemical properties of the bio-waste derived plastic-waste modified rejuvenators

4.1.1. GC-MS results

Fatty acids are typically composed of known compounds featuring 16–18 carbon atoms. When using Gas Chromatography-Mass Spectrometry (GC-MS) based on C16 and C18 standards, the compounds are expected to exhibit retention times of 18.39 and 20.21 minutes. However, in the case of Rej-A, lower molecular weight compounds were observed, as illustrated in Fig. 2. Conversely, the chromatograms for Rej-

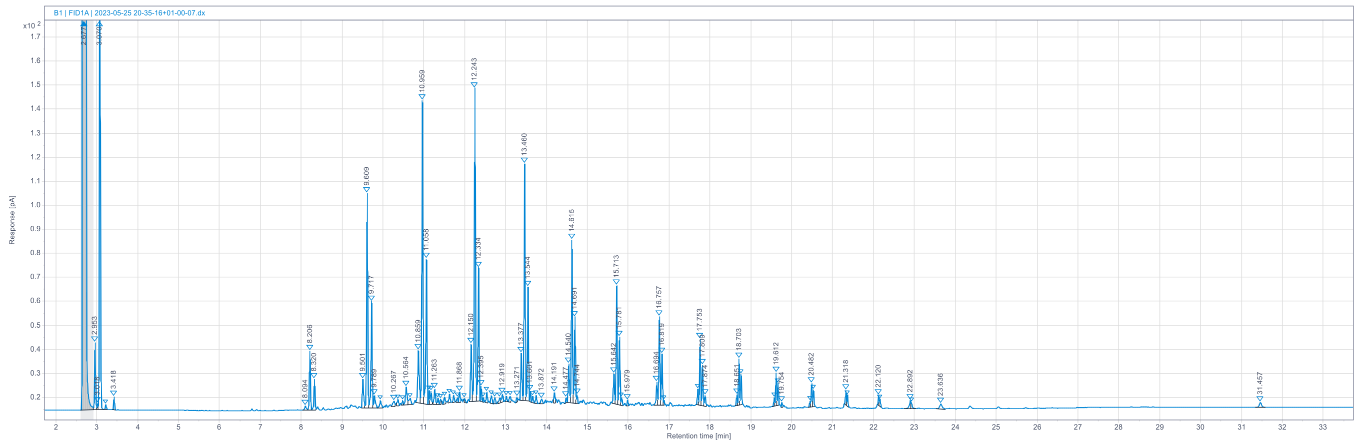


Fig. 2. GC-FIR results of Rej-A.

B revealed no fatty acids within these specified retention times, as depicted in Fig. 3. Previous studies reported that bio-rejuvenators with a high content of monounsaturated and stable and fatty acids exhibit better rejuvenation efficiency [46,47]. Therefore, quantifying fatty acid content can provide insight into performance changes exhibited by the rejuvenated binders. The absence of these fatty acids suggested that using these two rejuvenators might be less efficient compared to the purely bio-oil-based rejuvenators, therefore higher dosage might be required to achieve adequate performance [48].

4.1.2. Thermal stability of rejuvenators

To achieve an effective rejuvenation of aged bitumen, the rejuvenators are intended to have sufficient thermal stability to avoid evaporation during mixing and rejuvenation process. Therefore, it would be optimum if the degradation temperatures of bio-rejuvenator constituents are higher than the blending temperature of the rejuvenation process, which was 160 °C in this study. The thermogravimetric results of the rejuvenators are shown in Fig. 4.

The results for Rej-A revealed a 4 % mass loss between 30 °C and 100 °C during the initial heating cycle. Beyond 100 °C, there was a sharp decrease in the weight of Rej-A, resulting in an additional 15.6 % loss at 160 °C. By the end of the initial cycle at 250 °C, the total mass loss of Rej-A reached 43.46 %. This significant reduction in mass loss could be attributed to the presence of volatile components in the sample, likely including excess moisture found in the crude state of the pyrolysis specimen. Upon cooling back down to 30 °C, the sample experienced an additional 5.51 % mass loss, primarily occurring when the temperature dropped from 250 °C to 150 °C. In the second heating cycle, mass loss

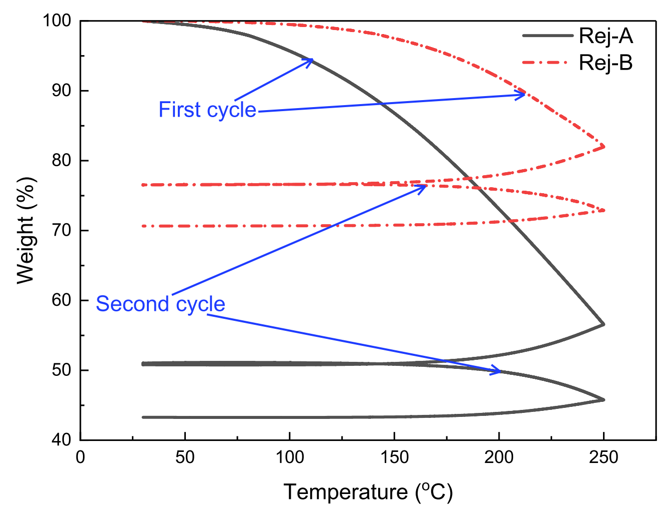


Fig. 4. TGA thermograph of rejuvenators for two cycles.

became negligible, totalling 5.27 %, as the evaporation of light components, such as moisture, had already occurred during the first cycle. The cumulative mass loss over two cycles amounted to 56.73 %. These findings suggested that when blending Rej-A with aged bitumen, temperature should be closely monitored and controlled. Notably, at a temperature of 150 °C, the mass loss was 13.16 %, while at 135 °C, the

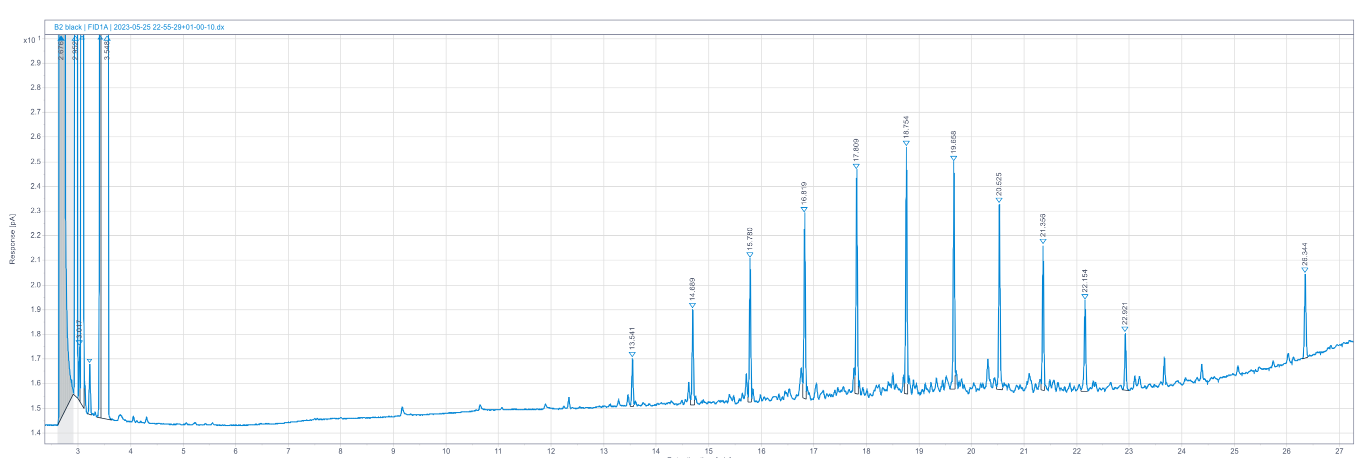


Fig. 3. GC-FIR results of Rej-B.

mass loss was only 9.96 %. Therefore, using dry treatments to remove moisture from Rej-A or implementing warm mix technology could maximise the rejuvenation efficiency of Rej-A [47].

In contrast, for Rej-B, the mass losses at the blending temperature (160 °C) and at the end of the first and second cycles were 3.3 %, 18.04 %, and 29.35 %, respectively. This was significantly lower than those for Rej-A. These observations were expected, as Rej-B is a filtered byproduct of Rej-A, with moisture and light components removed. The mass loss curves for the second cycles of both Rej-A and Rej-B were similar, indicating that most mass loss occurred during the initial heating process.

4.1.3. Differential scanning calorimetry (DSC)

DSC curves shed light on the thermal characteristics of materials, such as crystallisation/melting of wax and glass transition [49,50]. Fig. 5 shows the results of the DSC for the two bio-rejuvenators.

DSC results for Rej-A showed a gradual increase in endothermic heat flow during the first cycle, with a minor peak observed at 60 °C. This peak could be attributed to the melting of waxy components, while potential degradation peaks appeared when the temperature exceeded 200 °C. In the second cycle, only a smooth endothermic heat flow curve was visible, with no notable peaks. This suggested that the lighter components had evaporated, leaving behind only char-like components in the rejuvenator, thereby enhancing its thermal stability.

In contrast, the heat flow curves for Rej-B in both cycles displayed similar trends, differing from the results for Rej-A. A prominent peak appeared at approximately 90 °C, suggesting that at this temperature, the solid Rej-B melted into liquid. Therefore, temperatures above 90 °C should be sufficient for blending with Rej-B. The heat flow curves for both cycles were similar and nearly overlapped before the rejuvenator changed to liquid, indicating that the evaporation of lighter components in Rej-B was less significant compared to Rej-A.

4.1.4. Functional groups of rejuvenators

FTIR results for Rej-A and Rej-B are shown in Fig. 6. The spectra for both samples showed no significant differences in the number or location of peaks. The only notable variation existed in the area under the peak at a wavenumber of approximately 1640 cm $^{-1}$, which was linked to C═C stretching, such as alkenes. This observation suggests that Rej-B contains more alkenes than Rej-A. Apart from this observation, the spectra implied that the chemical composition of the pyrolysis oil remained consistent in FTIR analyses before and after the removal of light fractions and biochar. It confirmed that the extracted light volatile compounds and biochar content did not contribute to any detectable vibrational waves within the captured FTIR range.

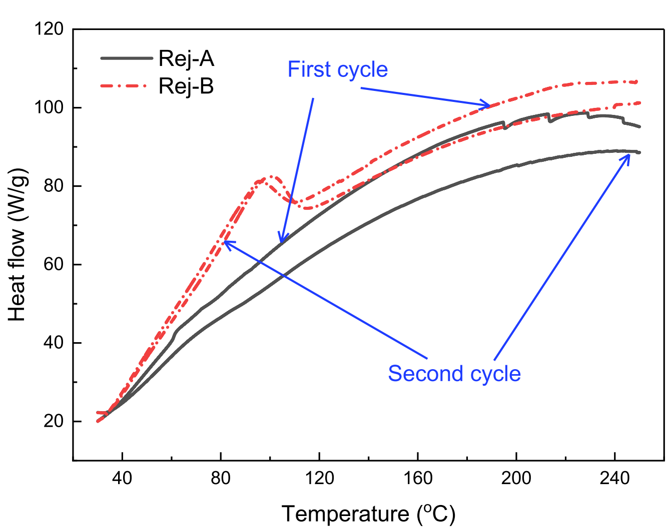


Fig. 5. DSC results for the rejuvenators.

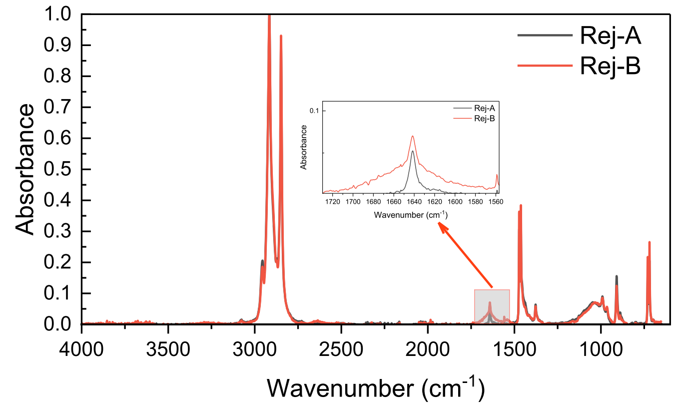


Fig. 6. Spectra for the rejuvenators.

The FTIR spectra revealed several functional groups in both Rej-A and Rej-B: C-H stretching in alkanes was observed at wavenumbers 2980–2800 cm^{-1}; C═C stretching from alkenes appeared at 1650–1580 cm^{-1}; C-H bending in alkanes was found at 1470–1350 cm^{-1}; O-H bending in alcohols occur at 1377.5 cm^{-1}; and in-plane C-H bending for aromatic and monosubstituted compounds were observed at 915–650 cm^{-1}.

4.2. Physiochemical properties of bitumen in terms of ageing and rejuvenation

4.2.1. Thermal stability

Thermogravimetric analysis was conducted on unaged, laboratory-aged, and rejuvenated bitumen samples using a consistent heating programme to compare their thermal behaviour. The mass losses observed for all binders after two cycles of heating and cooling are illustrated in Fig. 7. The code "RA" was used to denote bitumen rejuvenated using Rej-A, while "RB" referred to bitumen rejuvenated using Rej-B. The number after RA or RB refers to the mass percentage dosage of the rejuvenators. These codes were consistently used throughout in the remainder of the manuscript.

When examining thermogravimetric properties of bitumen, it was found that virgin bitumen exhibited the least significant mass loss, while bitumen rejuvenated with 18 % dosage of Rej-A displayed the most pronounced mass loss, which was 9.72 %. It is important to note that although aged binder showed a more obvious mass loss compared to virgin binder, this did not necessarily mean that the virgin binder is more thermally stable. The ultimate mass change in virgin binder

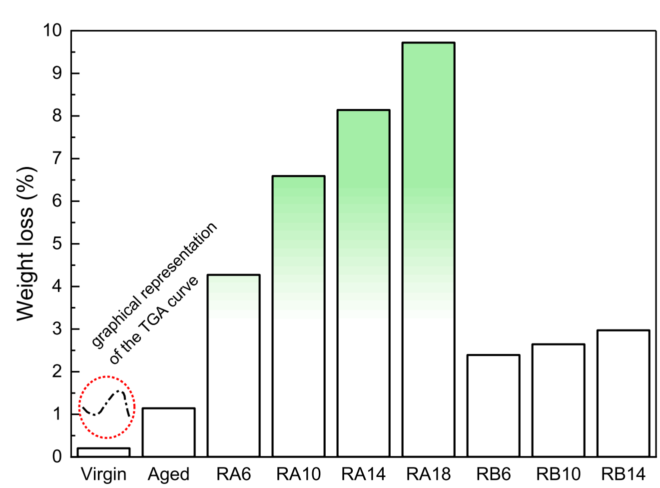


Fig. 7. Thermogravimetric Analysis of bitumen.

resulted from a combination of both mass gain and mass loss. Initially, the virgin binder experienced a gradual mass loss due to the evaporation of light components as the temperature increased. This was followed by a mass gain, attributed to oxidation from atmospheric gases. Finally, another mass loss occurred, likely due to the degradation of bitumen. In contrast, neither the aged nor the rejuvenated bitumen samples displayed any noticeable mass gain; they consistently lost mass during heating.

This mass loss in rejuvenated bitumen was largely dominated by the evaporation of the rejuvenators, especially Rej-A. The mass loss of rejuvenated bitumen with 6 %, 10 %, 14 % and 18 % dosages of Rej-A were 4.27 %, 6.59 %, 8.14 % and 9.72 %, respectively. The correlation between dosage and mass loss of rejuvenated bitumen suggested that the mass loss could be contributed to the evaporation of the moisture and other light components within Rej-A, which was proven in previous subsections. The mass loss of rejuvenated bitumen with Rej-B aligned with this observation.

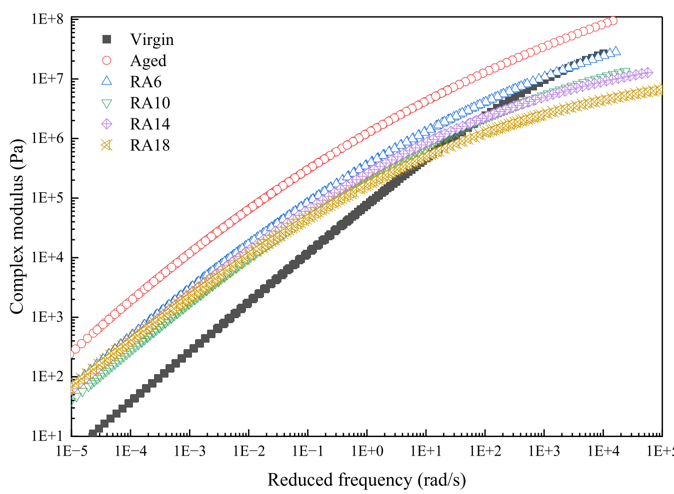
In summary, while the bitumen itself demonstrated relative thermal stability, the rejuvenators did not, which resulted in lower thermal stability in the rejuvenated bitumen. To achieve satisfactory rejuvenation, it is essential to stabilise the thermal properties of the rejuvenators. One approach to address this issue is the removal of volatile components from the rejuvenators. This method has been shown to be effective, as refining Rej-A to produce Rej-B resulted in a rejuvenator that is significantly more thermally stable.

4.2.2. Analysis based on master curves

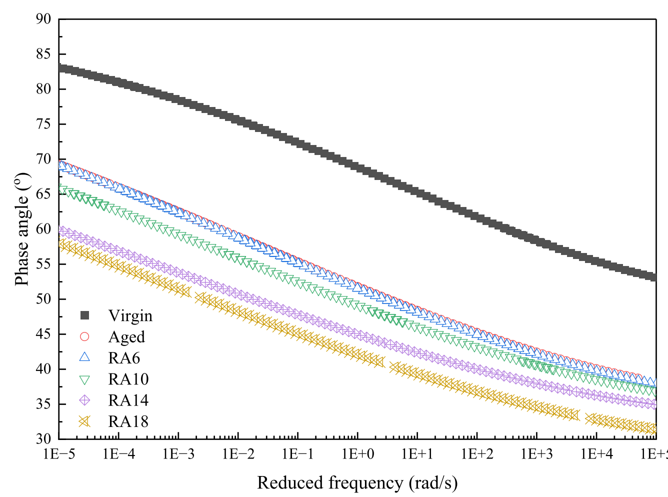
The master curves of complex modulus and phase angle of bitumen at virgin, aged and rejuvenated conditions are shown in Fig. 8. The reference temperature was 25 °C for all master curves.

Fig. 8 illustrated that Rej-A effectively softened aged bitumen. When comparing the master curves of virgin and aged binders, a significant difference was observed at low frequencies (which correspond to high temperatures). However, these master curves converged at high frequencies (equivalent to low temperatures). Given that aging-induced hardening at high temperatures enhances resistance to permanent deformation but impairs thermal cracking resistance at low temperatures, the goal of rejuvenation should be to reduce the stiffness of bitumen at low temperatures without excessively softening it at high temperatures.

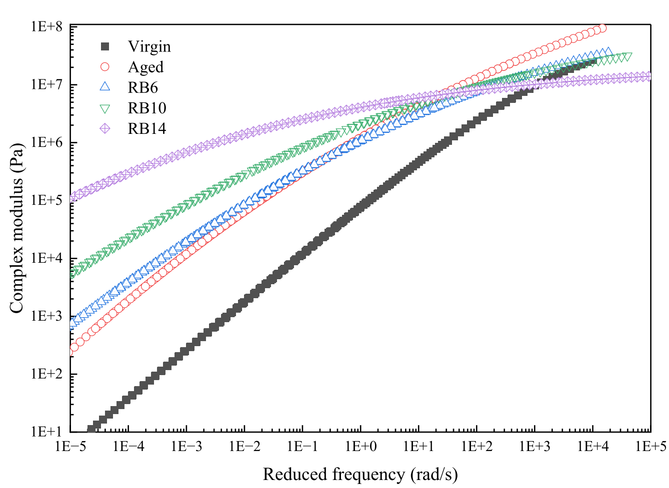
The master curves for rejuvenated binders exhibited different behaviour. At lower frequencies, the complex moduli of rejuvenated binders were higher than those of virgin binders but lower than those of aged binders. Interestingly, rejuvenated binders had very similar values of complex moduli at these low frequencies, irrespective of the dosage of rejuvenator used. However, the situation changed considerably at high frequencies: rejuvenated binders with higher dosages of rejuvenators tended to have significantly lower complex moduli than those with



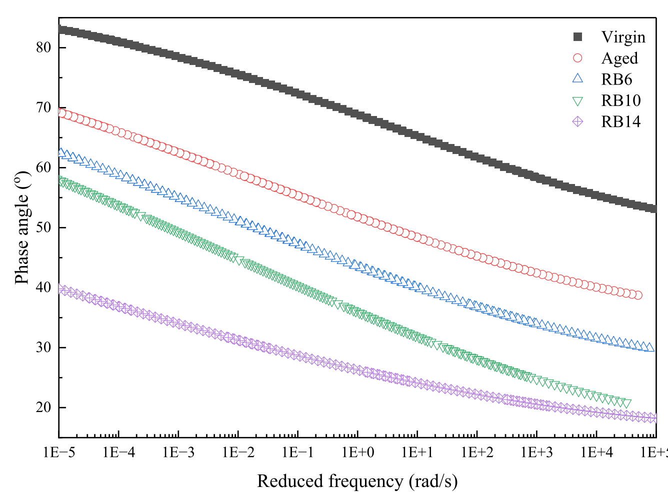
(a) Complex modulus for Rej-A rejuvenated bitumen



(b) Phase angle for Rej-A rejuvenated bitumen



(c) Complex modulus for Rej-B rejuvenated bitumen



(d) Phase angle for Rej-B rejuvenated bitumen

Fig. 8. Master curves of bitumen before ageing, after ageing, and after rejuvenation.

lower dosages, and the difference became more pronounced as the frequency increases. This indicated that the bio-rejuvenator can effectively restore the low-temperature performance of aged bitumen while compromising its high-temperature performance.

However, when examining the phase angle of the master curves, it became evident that rejuvenators faced challenges in restoring the viscoelastic balance of aged bitumen. The introduction of rejuvenators pushed the phase angle of rejuvenated bitumen in the same direction as ageing; that is, the phase angle decreased as the dosage increased. One plausible explanation for this is the evaporation of the lighter components of the rejuvenators. Certain oily components evaporate post-rejuvenation, leaving behind predominantly elastic components in the mixture, thus increasing the elasticity of the bitumen.

In contrast, master curves for binders rejuvenated with Rej-B differ significantly from those rejuvenated with Rej-A. At lower frequencies, the complex moduli of these rejuvenated binders were even higher than those of aged bitumen. However, at higher frequencies, their complex moduli were lower than both the aged and virgin binders. This could be attributed to the evaporation of lighter components at higher temperatures, and thereby dramatically increasing the complex moduli. Additionally, DSC results revealed that the melting point of Rej-B was around 90 °C, whereas the softening point of bitumen was around 45 °C. This indicated that at moderately high temperatures, such as 70 or 80 °C, the bitumen was in a liquid phase while Rej-B remained solid, leading to an increase in the complex modulus of the mixture. The complex modulus of bitumen was quite high at low temperatures, whereas Rej-B was less sensitive to temperature changes, resulting in a mixture whose complex modulus was lower than that of aged bitumen alone. It was thereby observed that the temperature sensitivity of binders decreased with the introduction of rejuvenators, as indicated by the reduced slope of the master curves. Overall, these rejuvenators effectively lowered the complex modulus of binders at lower temperatures without compromising their high-temperature performance too much. Consequently, these bio-rejuvenators showed promise in recovering the performance of binders that have deteriorated due to ageing.

4.2.3. Black space diagrams of binders

Black Space diagrams representing rheological data of bituminous materials in the form of complex modulus versus phase angle have been successfully used for the interpretation of material behaviour and performance, such as the durability which can be characterised using Glover-Rowe (G-R) parameter [51,52]. The G-R parameter for bitumen can be computed using the complex modulus and phase angle at the frequency of 0.005 rad/s and temperature of 15 °C, as per Eq. (1) [53].

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

The value of G-R parameter higher than 180 kPa is considered as the warning threshold for potential cracking in bitumen. Beyond this point, the cracking might initialise within bitumen while a value of 450 kPa is deemed as the limit at which significant cracking is likely to occur.

It can be observed from Fig. 9 that virgin binder was situated in a “safe zone”, indicating a low likelihood of durability issues. In contrast, ageing shifted the G-R parameter closer to the cracking zone, signalling onset of potential damage. The incorporation of Rej-A reversed this trend. This was further evidenced by a more stable complex modulus and a significant reduction in phase angle as dosages increase. However, the use of Rej-B introduced notable durability related risks. With increased dosages of Rej-B, the rejuvenated binders moved toward the critical cracking zone. Although none of the rejuvenated binders cross the cracking warning line, the data clearly indicated an increased risk of cracking potential. Therefore, while Rej-A appeared to mitigate durability risks, Rej-B seemed to exacerbate them to some extent.

In addition to the G-R parameter, this study also employed more conventional metrics like the SHRP fatigue parameter (G*sin δ) and rutting parameter (G*/sin δ). The fatigue parameter was calculated

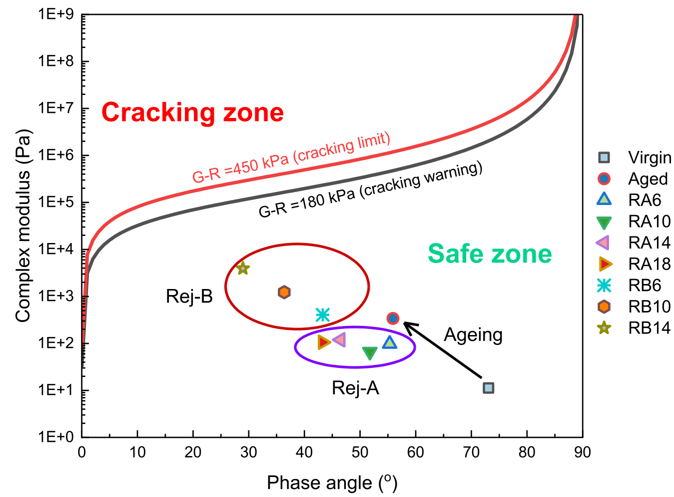


Fig. 9. Black space diagram with G-R parameter.

using the complex modulus and phase angle measured at 10 rad/s at an intermediate temperature. In this study, 20°C was chosen as the reference temperature. Similarly, the rutting parameter was derived from measurements taken at a high temperature, typically the same as the high PG grade. For this study, 70 °C was selected as the reference temperature for the rutting parameter. The Black Space diagram featuring both fatigue and rutting parameters are presented in Fig. 10.

The fatigue parameter has a prescribed limit of 5000 kPa; exceeding this threshold implies the material is likely to encounter durability issues. In this study, both virgin and Rej-A rejuvenated binders met this requirement with all binders residing in the “safe zone”. However, the binder aged for 40 hours using the PAV method did not meet the criterion, signalling a higher risk of fatigue issues after long term aging. Furthermore, binders rejuvenated by Rej-B resided in a high-risk zone as these binders were close to the critical limit. In terms of the rutting parameter, distinct limits are set for virgin (or rejuvenated) and RTFOT-aged binders. The rutting parameter should be no less than 1 kPa for virgin or rejuvenated binders, and no less than 2.2 kPa for RTFOT-aged binders. This study revealed that only the binder rejuvenated with an 18 % dosage of Rej-A failed to meet this criterion, indicating potential overdosing.

After rejuvenation, compared to aged binders, binders treated with both rejuvenators become softer, resulting in reduced rutting parameters. However, the ways these parameters decreased differ between them. For Rej-A rejuvenated binders, complex modulus decreased while

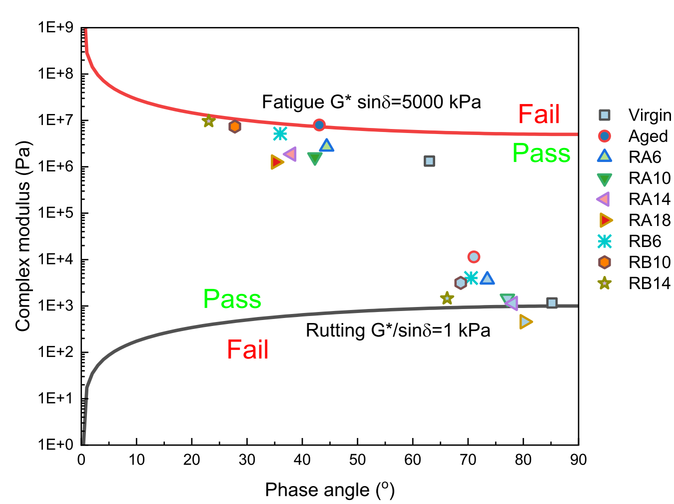


Fig. 10. Black Space with fatigue and rutting parameters.

phase angle increased. In terms of Rej-B rejuvenated bitumen, both complex modulus and phase angle decreased. Overall, the results suggested that introducing these rejuvenators compromised high-temperature performance of bitumen, but it was still within a reasonable limit when the dosages were lower than 14 %.

4.2.4. Characterisation of the high-temperature performance of rejuvenated bitumen

There are two main parameters used to illustrate the high-temperature performance of bitumen, namely non-recoverable compliance (J_{nr}) and recovery percent (*%R*) respectively, which can be computed using the raw data of strain. The strain against testing time plot is shown in

Fig. 11 showed a significant impact of ageing on reducing the strain of bitumen, while rejuvenation tended to have the opposite effect. Specifically, dotted lines represented strain versus time curves for binders rejuvenated by Rej-A, and dashed lines represented those rejuvenated by Rej-B. It was found that increased dosages resulted in higher strain of the rejuvenated bitumen. At the dosage of 14 %, both Rej-A and Rej-B effectively restored the high-temperature performance of aged bitumen to the level of virgin bitumen. However, the dosage of 18 % was excessive, leading to substantial permanent deformation issues. Results for the J_{nr} and *%R* parameters are further elucidated in Fig. 12.

Lower values of J_{nr} and higher values of *%R* are always desirable since they suggest better high-temperature performance. A lower J_{nr} implies greater resistance to deformation, while a higher *%R* suggests better recovery capabilities of the asphalt pavement after loading. It was seen from Fig. 12 that J_{nr} decreased while *%R* increased after ageing, favourably affecting resistance to permanent deformation or rutting. However, upon rejuvenation, the permanent deformation resistance of bitumen started to deteriorate with increasing dosages of rejuvenators. A dosage threshold around 12 % was identified for both Rej-A and Rej-B, as binders rejuvenated with a 10 % dosage exhibited lower J_{nr} values than virgin binders but showed higher values at a 14 % dosage.

To investigate the stress sensitivity of binders in terms of ageing and rejuvenation, the $J_{nr\text{-}diff}$ parameter, as defined in Eq. (2) was employed in this study, as shown in Fig. 13. It was observed that both ageing and rejuvenation followed a similar trend concerning the strain sensitivity of bitumen. Specifically, the sensitivity to strain increased with rising dosages of rejuvenators. Notably, binders rejuvenated with Rej-B showed higher strain sensitivity compared to those treated with Rej-A at equivalent dosages. Importantly, all tested binders met the AASHTO M19 requirement for $J_{nr\text{-}diff}$, which stipulates a limit of 75 %.

$$J_{nr-diff} = \frac{J_{nr3.2} - J_{nr0.1}}{J_{nr0.1}} \tag{2}$$

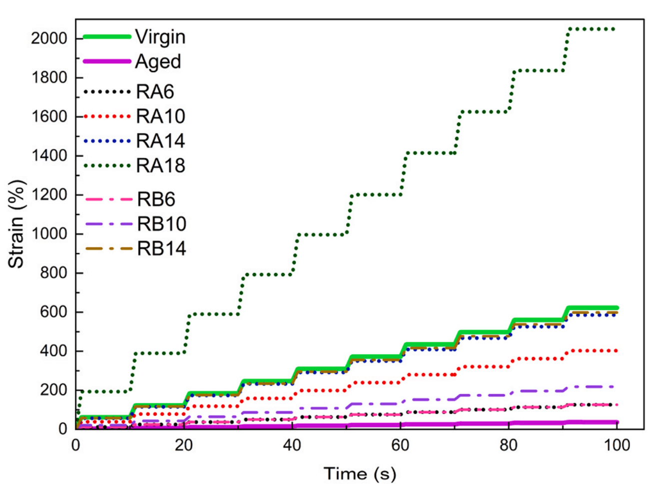


Fig. 11. Strain-time curves of binders at 3.2 kPa.

In summary, the incorporation of rejuvenators slightly compromised the high-temperature performance of bitumen. This results in binders that are less resistant to permanent deformation and more susceptible to strain sensitivity. However, maintaining the dosage of both rejuvenators below 14 % ensured that high-temperature performance remained within acceptable limits.

4.2.5. Fatigue performance of rejuvenated bitumen

The fatigue performance of bitumen can reflect the resistance to repeated loading at intermediate temperature. The stress-strain curves of binders measured by LAS tests before ageing, after ageing and after rejuvenated by two rejuvenators are shown in Fig. 14.

Fig. 14 indicates that the ageing process led to increased stress levels in bitumen compared to virgin binders when subjected to identical strain levels. The introduction of both Rej-A and Rej-B rejuvenators appeared to mitigate the differences between aged and virgin binders, although the correlation between dosages and stress levels is more complex.

For Rej-A, the relationship between dosage and stress reduction was not straightforward. At lower strain levels (below 20 %), a 10 % dosage of Rej-A yielded the most significant reduction in stress, while a 6 % dosage has the least impact. Interestingly, as the dosage increased, its effectiveness in reducing stress diminished. Once strain levels surpass 20 %, the stress curves intersected, although the 10 % dosage continues to display the most substantial stress-reducing effect. In the case of Rej-B, a higher dosage resulted in more significant stress reduction, but only for strain levels below 20 %. Beyond that, the stress curves for different dosages began to overlap, similar to that observed with Rej-A. The fatigue life of binders at the strain level of 2.5 % is shown in Fig. 15.

Fig. 15 highlighted the impact of ageing on the fatigue life of bitumen at a strain level of 2.5 %. It was revealed that ageing improved the fatigue performance of bitumen when the strain level was relatively low [54,55]. The introduction of rejuvenators to the aged bitumen extended the fatigue life of the binders. This effect was observed for both types of rejuvenators, although Rej-B led to a more dramatic increase in fatigue life. In addition to the commonly used 2.5 % strain level, the study also considered fatigue life at a 15 % strain level, which is thought to be more closely correlated with the fatigue life of asphalt mixtures [56]. The results for fatigue life at strain level of 15 % are presented in Fig. 16.

Results indicated that ageing adversely impacted the fatigue life of bitumen at the strain level of 15 %. However, rejuvenation successfully mitigated this decline. For both Rej-A and Rej-B, fatigue life increased as dosages increased up to 14 %. Beyond this point, notably at the dosage of 18 % for Rej-A, the fatigue life of the rejuvenated bitumen significantly reduced, suggesting an optimal dosage limit of 14 %.

5. Conclusions

This study comprehensively evaluated the feasibility of using municipal wastes derived bio-rejuvenators to restore the properties of aged bitumen. Two bio-rejuvenators were produced from municipal wastes using pyrolysis-based methods and used at various percentages for rejuvenating aged bitumen. Various chemical and rheological testing and analysis were carried out on the modified binders and the following conclusions could be drawn based on the results:

(1) Both bio-rejuvenators were generally effective in recovering the properties of aged bitumen. Out of the two, the crude polymer-based rejuvenator (Rej-A) outperformed the filtered wax-based rejuvenator (Rej-B) in recovering rheological properties. However, its lack of thermal stability might constrain its broad field applicability.

(2) The complex modulus of aged bitumen was effectively reduced by bio-rejuvenators while the viscoelastic balance (phase angle) could not be recovered to the initial value. Moreover, the high-temperature performance was slightly compromised.

(3) G-R parameter, SHRP fatigue parameter, and fatigue life suggested that Rej-A could effectively improve the fatigue performance of

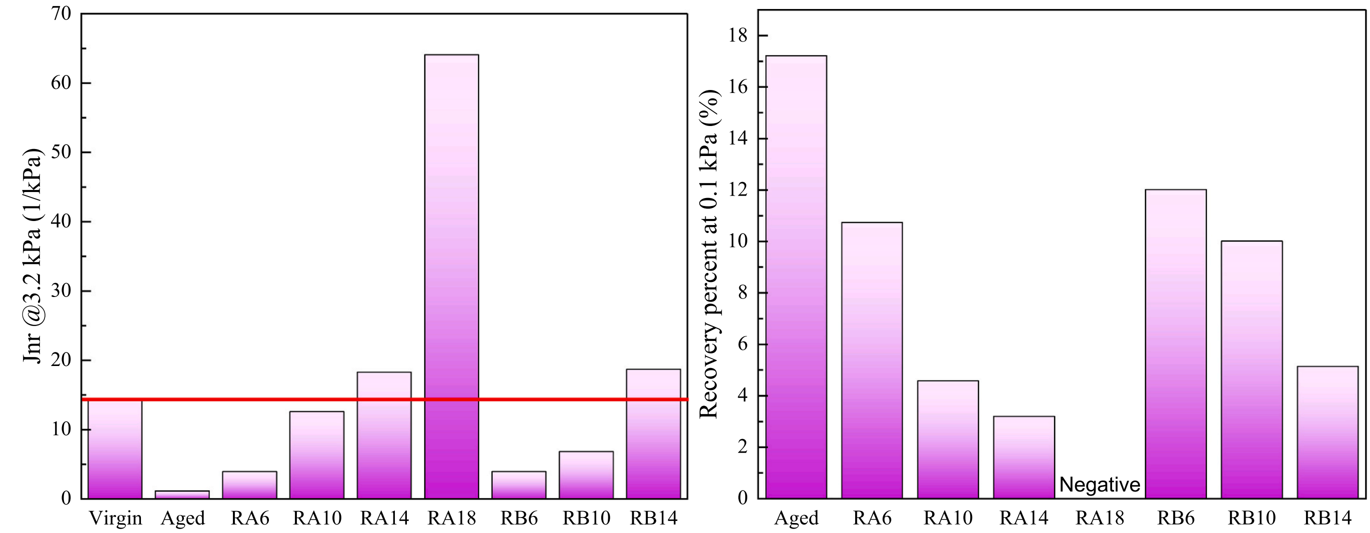


Fig. 12. High-temperature performance of bitumen (left: J_{nr}, right: *%R*).

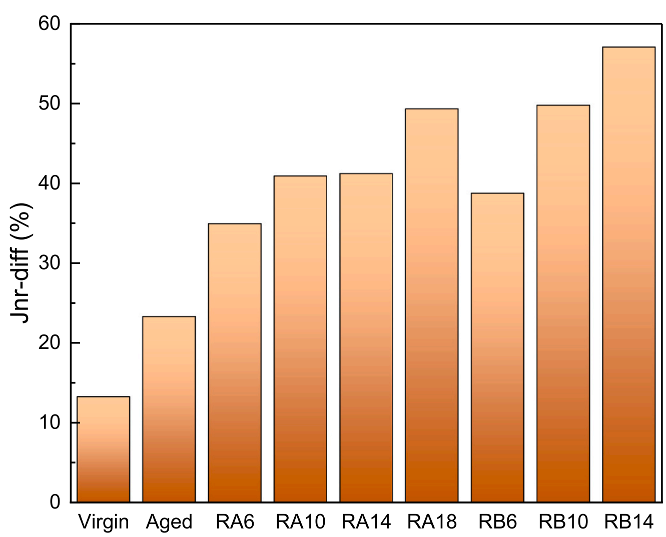


Fig. 13. The $J_{nr\text{-}diff}$ parameters for binders.

aged bitumen. However, G-R parameter suggested that Rej-B was detrimental to the fatigue performance of bitumen.

(4) Post-rejuvenation, modified bitumen exhibited increased strain sensitivity while showing a reduced sensitivity to temperature

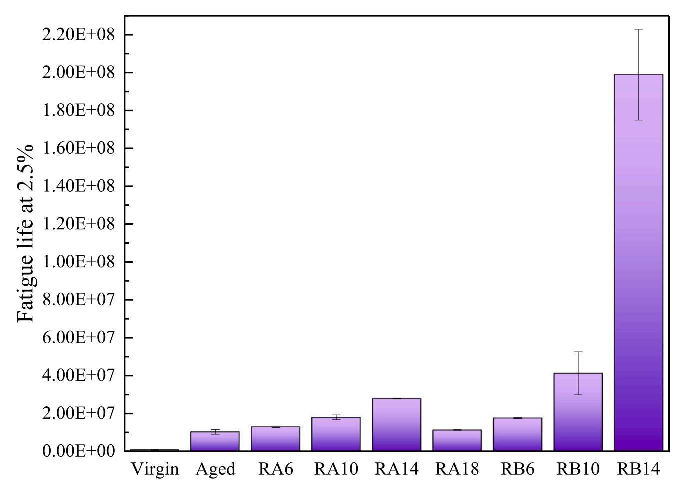


Fig. 15. Fatigue lives of binders at strain level of 2.5 %.

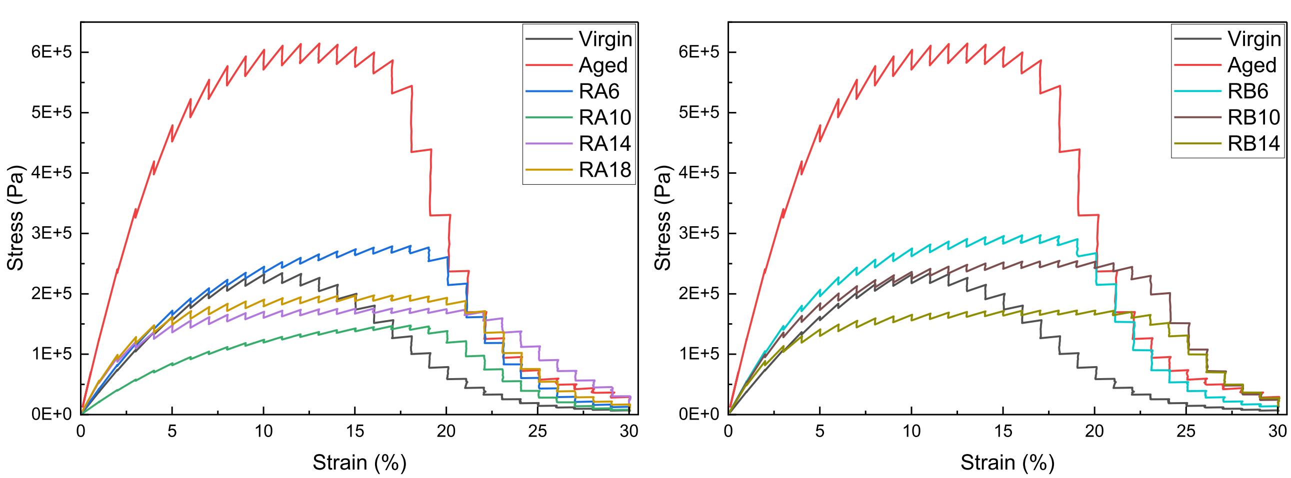


Fig. 14. Stress-strain curves of binders in terms of ageing and rejuvenation.

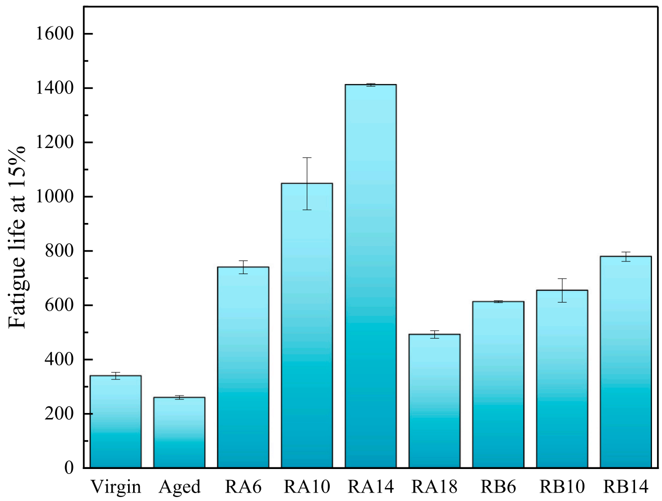


Fig. 16. Fatigue lives of binders at strain level of 15 %.

variations. This indicated a shift in the performance characteristics that should be accounted for in its application.

Overall, this study suggested that the bio-rejuvenators derived from municipal wastes were promising for recovering the properties of aged bitumen. However, there are still some limitations that warrant further investigation. Firstly, Rej-A was relatively unstable, it is suggested to improve its thermal stability using appropriate processing methods. Lastly, it is suggested to conduct more comprehensive rheological analysis for the modified binders including evaluating its low temperature performance and optimising dosages in relation to an overall balanced binder performance.

CRediT authorship contribution statement

Anand Sreeram: Writing – review & editing, Supervision, Investigation. **Miles Watkins:** Writing – review & editing. **Helen Bailey:** Writing – review & editing, Investigation. **Gordon Dan Airey:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **John Twitchen:** Writing – review & editing. **David Hughes:** Writing – review & editing, Resources, Investigation, Data curation. **Eman Omairey:** Writing – original draft, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Yongping Hu:** Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

Acknowledgements

This research is funded by Rees Jeffreys Road Fund. The first author would also like to express gratitude to the China Scholarship Council for providing financial support during the pursuit of his PhD degree under grant number of 202106560001. Special thanks are extended to Jonathan Watson, Martyn Barrett, Theo Ching, Paul Eloke and Dr Gillian Taylor for their invaluable technical assistance throughout the experimental phase of this research.

References

[1] F. Suwarto, T. Parry, G. Airey, Review of methodology for life cycle assessment and life cycle cost analysis of asphalt pavements, Road. Mater. Pavement Des. (2023) 1–27.

[2] D. Adwani, G. Pipintakos, J. Mirwald, Y. Wang, R. Hajj, M. Guo, M. Liang, R. Jing, A. Varveri, Y. Zhang, K. Pei, X. Xu, Z. Leng, D. Li, W. Villamil, S. Caro, E. Chailleux, J. Cantot, S. Weigel, J. Škultecké, G. Tarsi, A. Margaritis, H. Wang, Y. Hu, G. Airey, A. Sreeram, A. Bhasin, Examining the efficacy of promising antioxidants to mitigate asphalt binder oxidation: insights from a worldwide interlaboratory Investigation, Int. J. Pavement Eng. 25 (1) (2024) 2332363.

[3] C. Baek, B.S. Underwood, Y.R. Kim, Effects of oxidative aging on asphalt mixture properties, Transp. Res. Rec. 2296 (1) (2012) 77–85.

[4] F. Gu, X. Luo, Y. Zhang, R.L. Lytton, Using Overlay Test to Evaluate Fracture Properties of Field-Aged Asphalt Concrete, Constr. Build. Mater. 101 (2015) 1059–1068.

[5] Y. Hu, W. Si, X. Kang, Y. Xue, H. Wang, T. Parry, G.D. Airey, State of the art: multiscale evaluation of bitumen ageing behaviour, Fuel 326 (2022) 125045.

[6] I. Menapace, L.G. Cucalon, F. Kaseer, E. Masad, A.E. Martin, Application of low field nuclear magnetic resonance to evaluate asphalt binder viscosity in recycled mixes, Constr. Build. Mater. 170 (2018) 725–736.

[7] F.C. Thyrion, Chapter 16 asphalt oxidation, in: T.F. Yen, G.V. Chilingarian (Eds.), Developments in Petroleum Science, Elsevier, 2000, pp. 445–474.

[8] D. Lesueur, The Colloidal Structure of Bitumen: consequences on the Rheology and on the Mechanisms of Bitumen Modification, Adv. Colloid Interface Sci. 145 (1) (2009) 42–82.

[9] J.F. Masson, P. Collins, G. Polomark, Steric hardening and the ordering of asphaltenes in bitumen, Energy Fuels 19 (1) (2005) 120–122.

[10] A. Subhy, G.M. Pires, D. Lo Presti, G. Airey, The effects of laboratory ageing on rheological and fracture characteristics of different rubberised bitumens, Constr. Build. Mater. 180 (2018) 188–198.

[11] Y. Hu, W. Xia, Y. Xue, P. Zhao, X. Wen, W. Si, H. Wang, L. Zhou, G.D. Airey, Evaluating the ageing degrees of bitumen by rheological and chemical indices, Road. Mater. Pavement Des. (2023).

[12] J. Mirwald, S. Werkovits, I. Camargo, D. Maschauer, B. Hofko, H. Grothe, Understanding bitumen ageing by investigation of its polarity fractions, Constr. Build. Mater. 250 (2020) 118809.

[13] Y. Hu, H. Wang, L. Zhou, G.D. Airey, Towards an enhanced understanding of the functional groups within bitumen during ageing processes. Advances in Functional Pavements, CRC Press, 2024, pp. 83–87.

[14] G. Cuciniello, P. Leandri, S. Filippi, D. Lo Presti, G. Polacco, M. Losa, G. Airey, Microstructure and rheological response of laboratory-aged sbs-modified bitumens, Road Mater. Pavement Des. 22 (2) (2021) 372–396.

[15] H. Soenen, J. Besamusca, H.R. Fischer, L.D. Poulikakos, J.-P. Planche, P.K. Das, N. Kringos, J.R.A. Grenfell, X. Lu, E. Chailleux, Laboratory investigation of bitumen based on round Robin Dsc and Afm tests, Mater. Struct. 47 (7) (2013) 1205–1220.

[16] N. Harris, D. Shah, Net zero highways: our 2030/2040/2050 Plan, in: N. Highways (Ed.) London, 2021.

[17] M. Dare, M. Wilson, Net zero roadmap for concrete steel and asphalt, in: N. Highways (Ed.) London, 2022.

[18] H. Xu, Y. Zou, G. Airey, H. Wang, H. Zhang, S. Wu, A. Chen, Wetting of bio-rejuvenator nanodroplets on bitumen: a molecular dynamics investigation, J. Clean. Prod. (2024) 141140.

[19] Y. Hu, J. Ryan, A. Sreeram, M. Allanson, A.R. Pasandín, L. Zhou, B. Singh, H. Wang, G.D. Airey, Optimising the dosage of bio-rejuvenators in asphalt recycling: a rejuvenation index based approach, Constr. Build. Mater. 433 (2024).

[20] A. Behnood, Application of rejuvenators to improve the rheological and mechanical properties of asphalt binders and mixtures: a review, J. Clean. Prod. 231 (2019) 171–182.

[21] C. Chen, J. Lu, T. Ma, Y. Zhang, L. Gu, X. Chen, Applications of vegetable oils and their derivatives as bio-additives for use in asphalt binders: a review, Constr. Build. Mater. 383 (2023) 131312.

[22] K. Shi, F. Ma, Z. Fu, R. Song, D. Yuan, A.W. Ogbon, Enhancing aged Sbs-modified bitumen performance with unaged bitumen additives, Constr. Build. Mater. 412 (2024) 134768.

[23] E. Omairey, D. Hughes, Y. Hu, G. Airey, Feasibility evaluation of bio-waste derived, plastic-waste modified binder rejuvenators. Advances in Functional Pavements, CRC Press, 2024, pp. 58–61.

[24] Y. Hu, A. Sreeram, W. Xia, H. Wang, L. Zhou, W. Si, G.D. Airey, Use of hansen solubility parameters (hsp) in the selection of highly effective rejuvenators for aged bitumen, Road. Mater. Pavement Des. (2024) 1–19.

[25] Y. Yang, Y. Zhang, E. Omairey, J. Cai, F. Gu, A.V. Bridgwater, Intermediate pyrolysis of organic fraction of municipal solid waste and rheological study of the pyrolysis oil for potential use as bio-bitumen, J. Clean. Prod. 187 (2018) 390–399.

[26] C. Abdy, Y. Zhang, J. Wang, Y. Yang, I. Artamendi, B. Allen, Pyrolysis of polyolefin plastic waste and potential applications in asphalt road construction: a technical review, Resour., Conserv. Recycl. 180 (2022) 106213.

[27] C. Abdy, Y. Zhang, J. Wang, Y. Cheng, I. Artamendi, B. Allen, Investigation of high-density polyethylene pyrolyzed wax for asphalt binder modification: mechanism, thermal properties, and ageing performance, J. Clean. Prod. 405 (2023) 136960.

[28] U.K Department for Environment Food & Rural Affairs, Advanced Biological Treatment of Municipal Solid Waste, London, 2013.

[29] A. Rajib, S. Saadeh, P. Katawal, B. Mobasher, E.H. Fini, Enhancing biomass value chain by utilizing biochar as a free radical scavenger to delay ultraviolet aging of bituminous composites used in outdoor construction, Resour., Conserv. Recycl. 168 (2021) 105302.

[30] M. Zadshir, S. Hosseinnezhad, E.H. Fini, Deagglomeration of oxidized asphaltenes as a measure of true rejuvenation for severely aged asphalt binder, Constr. Build. Mater. 209 (2019) 416–424.
[31] W. Wu, M.C. Cavalli, W. Jiang, N. Kringos, Differing perspectives on the use of high-content sbs polymer-modified bitumen, Constr. Build. Mater. 411 (2024) 134433.
[32] BSI, Bitumen and Bituminous Binders. Determination of the Resistance to Hardening under Influence of Heat and Air. Rtfot Method, BSI London, UK, 2014.
[33] BSI, Bitumen and Bituminous Binders. Accelerated Long-Term Aging Conditioning by a Pressure Aging Vessel (Pav), BSI London, UK, 2014.
[34] P. Lin, X.Y. Liu, P. Apostolidis, S. Erkens, S.S. Ren, S. Xu, T. Scarpas, W.D. Huang, On the rejuvenator dosage optimization for aged Sbs modified bitumen, Constr. Build. Mater. 271 (2021).
[35] S.M. Saeed, M.H. Sutanto, M. Napiah, A. Usman, A. Batari, M.Y. Aman, N.S. A. Yaro, Optimization of rubber seed oil content as bio-oil rejuvenator and total water content for cold recycled asphalt mixtures using response surface methodology, Case Stud. Constr. Mater. 15 (2021).
[36] E.L. Omairey, Y. Zhang, F. Gu, T. Ma, P. Hu, R. Luo, Rheological and fatigue characterisation of bitumen modified by anti-ageing compounds, Constr. Build. Mater. 265 (2020) 120307.
[37] M. Elkashef, R.C. Williams, E. Cochran, Thermal stability and evolved gas analysis of rejuvenated reclaimed asphalt pavement (rap) bitumen using thermogravimetric analysis–fourier transform infrared (Tg–Ftir), J. Therm. Anal. Calorim. 131 (2) (2018) 865–871.
[38] A. Abdelaziz, E. Masad, A. Epps Martin, E. Arámbula-Mercado, A. Bajaj, Thermal, microscopic, and rheological characterization of rejuvenated asphalt binders, Mater. Struct. 55 (3) (2022) 98.
[39] P. Cong, J. Wang, Z. Zhou, H. Zhang, Preparation of rejuvenating agent and property evaluation of rejuvenated Sbs modified asphalt binders, Constr. Build. Mater. 233 (2020) 117911.
[40] P. Caputo, S. Eskandarsefat, M. Porto, V. Loise, A.A. Abraham, P. Calandra, L. Venturini, C.O. Rossi, Effect and mechanism of rejuvenation of field-aged bitumen extracted from reclaimed asphalt pavement, Transp. Res. Procedia 69 (2023) 863–870.
[41] S. Xie, X. Qin, Y. Cheng, D. Laskar, W. Qiao, S. Sun, L.H. Reyes, X. Wang, S.Y. Dai, S.E. Sattler, K. Kao, B. Yang, X. Zhang, J.S. Yuan, Simultaneous Conversion of all cell wall components by an oleaginous fungus without chemi-physical pretreatment, Green Chem. 17 (3) (2015) 1657–1667.
[42] S. Xie, S. Sun, S.Y. Dai, J. S.Yuan, Efficient coagulation of microalgae in cultures with filamentous fungi, Algal Res. 2 (1) (2013) 28–33.
[43] AASHTO, Estimating fatigue resistance of asphalt binders using the linear amplitude sweep, American Association of State Highway and Transportation Officials, Washington D.C., 2020.
[44] BSI, Bitumen and Bituminous Binders. Multiple Stress Creep and Recovery Test (Mscrt), BSI London, UK, 2015.
[45] J. Mirwald, D. Nura, B. Hofko, Recommendations for handling bitumen prior to Ftir spectroscopy, Mater. Struct. 55 (2) (2022) 26.
[46] F. Zhou, P. Karki, S. Xie, J.S. Yuan, L. Sun, R. Lee, R. Barborak, Toward the development of performance-related specification for bio-rejuvenators, Constr. Build. Mater. 174 (2018) 443–455.
[47] R.Bin Ahmed, K. Hossain, R.M. Hajj, Chemical, morphological, and fundamental properties of rejuvenated asphalt binders, J. Mater. Civ. Eng. 33 (2) (2021).
[48] S. Ren, X. Liu, S. Erkens, P. Lin, Y. Gao, Multi-Component Analysis, Molecular Model Construction, and Thermodynamics Performance Prediction on Various Rejuvenators of Aged Bitumen, J. Mol. Liq. 360 (2022) 119463.
[49] X. Lu, H. Soenen, P. Sjövall, G. Pipintakos, Analysis of asphaltenes and maltenes before and after long-term aging of bitumen, Fuel 304 (2021) 121426.
[50] H. Soenen, J. Besamusca, L.D. Poulikakos, J.-P. Planche, P.K. Das, N. Kringos, J. Grenfell, E. Chailleux, DifferentiaL Scanning Calorimetry Applied to Bitumen: Results of the Rilem Nbm Tg1 Round Robin test, in: N. Kringos, B. Birgisson, D. Frost, L. Wang (Eds.), Multi-Scale Modeling and Characterization of Infrastructure Materials, Springer Netherlands, Dordrecht, 2013, pp. 311–323.
[51] G.D. Airey, Use of black diagrams to identify inconsistencies in rheological data, Road. Mater. Pavement Des. 3 (4) (2011) 403–424.
[52] G.D. Airey, G.M. Rowe, J.E. Sias, H. Di Benedetto, C. Sauzeat, E.V. Dave, BlacK Space Rheological Assessment of Asphalt Material Behavior, J. Test. Eval. 50 (2) (2022).
[53] G.M. Rowe, G. King, M. Anderson, The influence of binder rheology on the cracking of asphalt mixes in airport and highway projects, J. Test. Eval. 42 (5) (2014) 1063–1072.
[54] Y. Hu, A. Sreeram, G.D. Airey, B. Li, W. Si, H. Wang, Comparative analysis of time sweep testing evaluation methods for the fatigue characterisation of aged bitumen, Constr. Build. Mater. 432 (2024) 136698.
[55] W. Wu, W. Jiang, J. Xiao, D. Yuan, T. Wang, X. Ling, Investigation of Las-based fatigue evaluation methods for high-viscosity modified asphalt binders with high-content polymers, Constr. Build. Mater. 422 (2024) 135810.
[56] H. Chen, H.U. Bahia, Proposed asphalt binder fatigue criteria for various traffic conditions using the Las or the G-R parameters, Mater. Struct. 55 (1) (2022) 24.