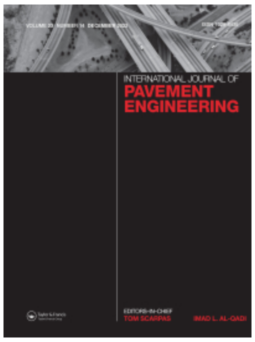

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Characterisation of bitumen through multiple ageing-rejuvenation cycles

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ABSTRACT

The multiple recycling of bitumen offers the possibility of reusing it for repeated lifecycles and achieve a higher degree of circularity of materials used in pavement construction. Aiming to identify the prospect, this study aged bitumen in a laboratory setting and then rejuvenated it using a bio-based rejuvenator for four ageing cycles. The low temperature and fatigue performance of the bitumen in each cycle was comprehensively characterised using dynamic shear rheometer (DSR) based rheological measurements. The results illustrated that although rejuvenation cannot recover all properties of the aged bitumen to the level of virgin bitumen, using rejuvenators can largely improve most properties negatively affected by ageing. The optimal dosage of rejuvenators should be determined based on the balance of the properties. The use of rejuvenation indexes, such as the one employed in this study, can assure that the low-temperature and intermediate temperature performance can be met through multiple ageing-rejuvenation cycles. In terms of chemical changes, although ageing reduces the chemical or colloidal stability of bitumen, rejuvenation can recover this property to its initial level. Overall, the results obtained in the study suggest that using appropriate rejuvenators, bitumen can potentially be recycled through multiple lifecycles.

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Bitumen; ageing; rejuvenation; rheology; multiple recycling

1. Introduction

Due to the combined effects of temperature, reactive oxygen species (ROS), UV and visible radiation etc., bitumen within asphalt mixtures gets oxidated and aged (Mirwald *et al.* 2020a). This inevitably leads to significant deterioration of its performance and usability (Davis and Petersen 1966). Aging results in significant physical and chemical changes in the properties of binders. Physically, the ageing of binders is associated with reduced penetration, ductility, viscoelastic balance (phase angle), together with increased stiffness, softening point and viscosity (Petersen *et al.* 1993). These changes generally lead to better resistance in rutting and decreased resistance to fatigue and thermal cracking (Subhy *et al.* 2018, Hu *et al.* 2022, Adwani *et al.* 2024). Chemically, the ageing of bitumen results in a reduction in the content of aromatics and the increase of asphaltenes, inducing instability of the colloidal system of the binder (Lesueur 2009, Hu *et al.* 2024). The increase in the formation of carbonyl and sulfoxide related functional groups acts as the fingerprints of ageing and show an increasing trend with higher levels of ageing (Mirwald *et al.* 2020b). Ageing also leads to a trend of increasing molecular weight within bitumen, which contributes to an increase in viscosity (Lu *et al.* 2021). Thermally, the glass transition temperature increases after ageing, caused by the increase of the content of asphaltenes (Soenen *et al.* 2014). Morphologically, the aggregation of asphaltenes results in a change in the roughness of the bitumen surface and the possible formation of 'bee-like' structures (Loeber *et al.* 1998). It can be concluded that the ageing of bitumen is an intricate phenomenon which ultimately results in the deterioration of performance and distresses of asphalt pavements (Alam *et al.* 2022, Sreeram *et al.* 2022).

Ageing of bitumen causes significant deterioration of the performance of asphalt pavements, leads to distresses like thermal cracking, fatigue cracking, stripping, potholes etc.(Ogbo *et al.* 2019, Ali *et al.* 2022). When the distresses are serious enough, pavements then need to be milled, resulting in materials that are as termed as reclaimed asphalt pavement (RAP). Using RAP in new pavement construction is now a necessity to achieve high levels of material circularity in pavements (Aurangzeb *et al.* 2014, De Pascale *et al.* 2023). However, the bitumen present in RAP is aged, therefore some measures need to be taken to recover the properties of aged bitumen to ensure that new mixtures meet mix target requirements (Kodippily *et al.* 2016, Abdelaziz *et al.* 2021, Xu *et al.* 2022). Rejuvenation of bitumen using chemical agents called 'rejuvenators' is a possible solution for recovering the properties of aged binder and thereby improve the performance of new pavements with high RAP content (Aurangzeb *et al.* 2014). Using rejuvenators can increase the use of RAP in new asphalt pavements as it softens the bitumen and improves its workability (Jamal *et al.* 2020). Rejuvenators such as bio-

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products, very soft bitumen, waste cooking oils, waste engine oils, tall oils, aromatic extracts, etc. have been commonly employed and tested in various field and laboratory applications (Cavalli *et al.* 2019). The rejuvenation mechanism is theorised to mainly include the supplementation of light fractions of bitumen (such as maltenes) and dissolution of asphaltenes (Kodippily *et al.* 2016). Apart from the selection of suitable rejuvenators, the determination of optimum dosages is another vital factor affecting the rejuvenation effectiveness (Zaumanis *et al.* 2014). The approaches for rejuvenator dosage optimisation include targeted penetration, viscosity, viscoelastic properties, and chemical analysis (Zaumanis *et al.* 2014, Zahoor *et al.* 2021). Generally, it is accepted that the correct utilisation of rejuvenators can effectively rejuvenate the aged bitumen, thereby recovering or even improving its performance. Recycling the aged bitumen in RAP efficiently using rejuvenators promotes the circularity of road pavements by the means of reducing the consumption of natural resources. In that respect, repeated recycling of bitumen through multiple lifecycles can facilitate this circularity to a higher level (Schwettmann *et al.* 2023).

Though there is considerable research related to the rejuvenation of aged bitumen, the long-term performance of rejuvenated bitumen especially when considering multiple cycles of ageing and rejuvenation is still not well understood and investigated (Makowska *et al.* 2017). Most of the current research focuses on different types of rejuvenators and their performance evaluation after one-time rejuvenation (Taherkhani and Noorian 2020, Abdelaziz *et al.* 2021, Zahoor *et al.* 2021, Xu *et al.* 2022). Few studies have investigated multiple cycles of rejuvenation and consequently, only limited results are available. Moreover, these studies mainly investigated up to two cycles of rejuvenation rather than multiple cycles, and the performance evaluation conducted was mostly simplistic (Makowska *et al.* 2017, Koudelka *et al.* 2019, Bocci *et al.* 2022). To address this concern, this study performed a comprehensive laboratory-based investigation into performance of bitumen through multiple cycles of ageing and rejuvenation to fully comprehend its associated rheological and chemical changes.

2. Scope

This study explored the possibility of repetitive recycling of aged bitumen to increase the circularity of asphalt pavements. Bitumen was aged in a laboratory and then rejuvenated using a bio-rejuvenator. The rejuvenated bitumen was then re-aged and re-rejuvenated again for four cycles. Comprehensive rheological tests, including frequency sweep (FS) tests, linear amplitude sweep (LAS) tests and low-temperature DSR tests with 4 mm geometry were carried out to comprehensively evaluate the performance of bitumen after each cycle of ageing and rejuvenation. The generic polarity-based fractions, saturates, aromatics, resins and asphaltenes (SARA) of bitumen after multiple cycles of ageing and rejuvenation were also measured using thin-layer chromatography with flame ionization detection (TLC-FID) technique to identify the chemical changes of bitumen during the whole recycling process. The results were then used to evaluate the possibility of recycling bitumen through multiple life cycles. Overall, the work conducted is expected to shed significant insights into possibility of multiple recycling of bitumen and help guide material selection and testing approaches in the future.

3. Materials and methods

3.1 Materials

The bitumen used in this study was a 70/100 penetration grade bitumen (unmodified) with a penetration of 81 (0.1 mm) and softening point of 45.4°C. The performance grade of this bitumen was PG 70-22. The rejuvenator used in this study was a bio-based commercial product. It is a dark-coloured liquid with hydrocarbon odour, as shown in Figure 1, with the density of 0.89 kg/l and the viscosity of 60 cP at 25°C.

3.2. Methodologies

3.2.1. Ageing and rejuvenation procedures

The virgin bitumen was aged in a laboratory using a rolling thin film oven (RTFO) at 163°C for 75 mins in accordance with BS EN 12607-1. The residue was subsequently subjected to pressure ageing vessel (PAV) ageing at 100°C and 2.1 MPa for 20 hours in accordance with BS EN 14769. Every batch of aged bitumen was poured into a large container and blended using a mixer at 160°C and 3000 r/min for 10 minutes to ensure homogeneity. The aged bitumen was rejuvenated using the bio-rejuvenator and then subjected to other cycles of re-ageing and re-rejuvenating as shown in Figure 2. The letter ‘V’ refers to the virgin binder and the aged binder is represented by letter ‘A’. Subsequently, 50 grams of aged bitumen was extracted from the large container and poured into a small container, then 1.5 grams (3% by the weight of aged bitumen) of the rejuvenator was added then blended for 10 mins at 160°C. Additionally, 2 and 2.5 grams of rejuvenator was added to another 50 grams of aged bitumen to get dosages of 4% and 5% respectively. The initial dosages of 3%, 4% and 5% were chosen following the manufacturer’s manual. The rejuvenated bitumen was labelled as AR + 3%, AR + 4% and AR + 5% respectively. Afterwards, the optimal dosage was determined based on the rejuvenation index, which will be introduced in the next subsection. Then, the rejuvenated

Figure 1. Rejuvenator used in this study.

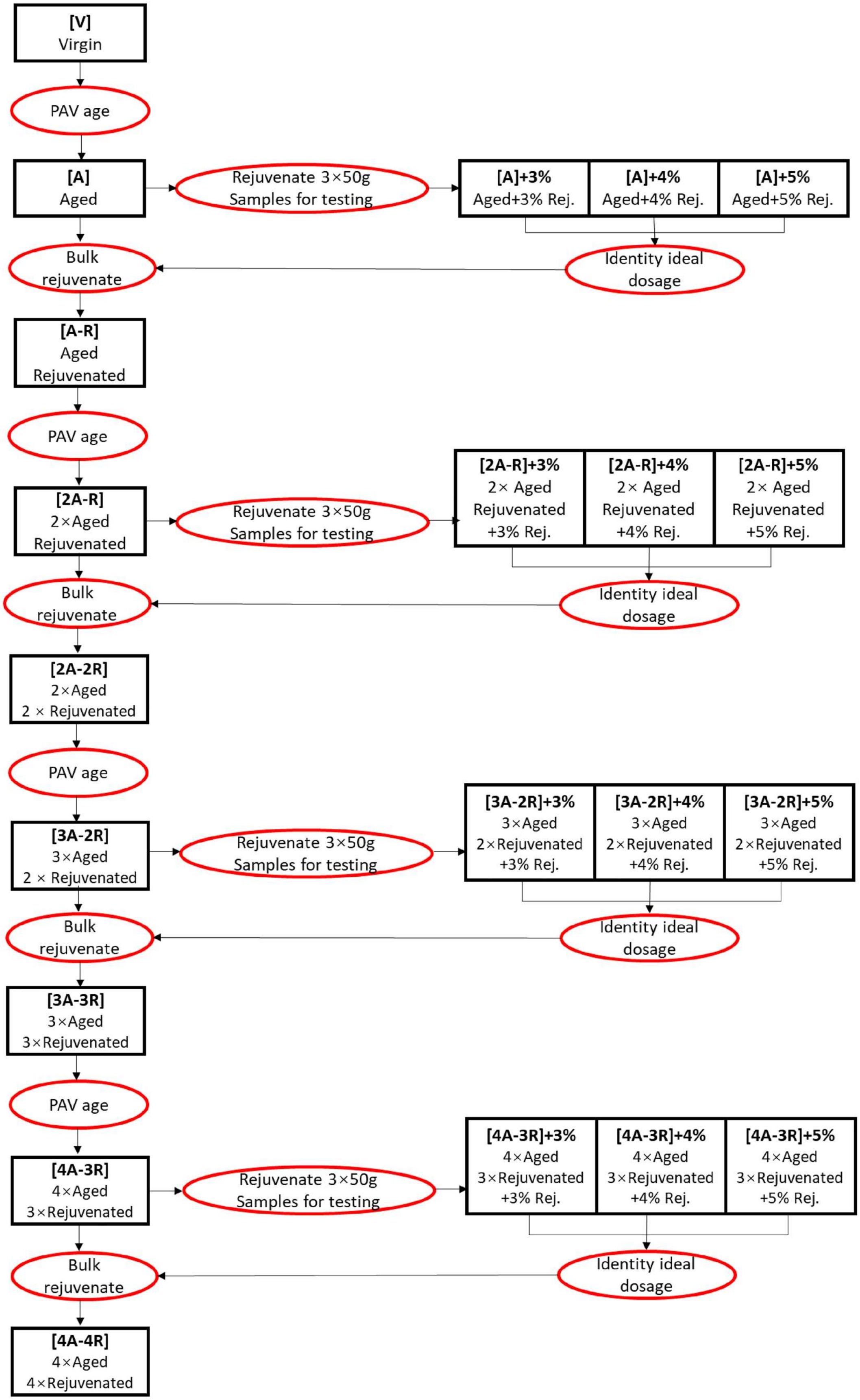


Figure 2. Programme of multiple cycles of ageing and rejuvenation.

bitumen with the optimal dosage of rejuvenator, labelled as bulk rejuvenate in Figure 2, was re-aged again and re-rejuvenated again until the fourth cycle.

3.2.2. Dosage optimisation

To determine the optimal dosage of rejuvenator, all binders were subjected to DSR frequency sweep tests at a constant strain level of 0.2% to ensure the linear viscoelastic (LVE) response of the bitumen over the temperature range of 10–70°C at intervals of 10°C and frequencies ranging from 0.1 rad/s to 100 rad/s with 10 frequencies per decade (Wang *et al.* 2020). The DSR test geometry configuration consisted of 25 mm parallel plates with a gap of 1 mm.

The master curves of complex modulus *(G*)* and phase angle (δ) were subsequently produced at a reference temperature of 25°C using the modified Christensen – Anderson – Marasteanu (CAM) model (Bahia *et al.* 2001), as shown in Equations (1) and (2). The Excel built-in function Solver was employed to automatically calculate the fitting parameters.

$$G* = \frac{G_g^*}{[1+(f_c/f_r)^k]^{m/k}} \tag{1}$$

$$\delta = 90I - \frac{90I - \delta_m}{\left\{1 + \left[\frac{\log\left(\frac{f_d}{f_r}\right)}{R_d}\right]^2\right\}^{\frac{m_d}{2}}} \tag{2}$$

Where, G^*_g = glass complex modulus; f_c = crossover frequency; f_r = reduced frequency; m,k = fitting parameters; δ_m = phase angle constant at f_d; f_d = location parameter with dimension of frequency, the value at the inflexion for binders; R_d, m_d = shape parameters; $I = 0$ if $f > f_d$, $I = 1$ if $f \le f_d$.

To identify the rejuvenation effectiveness and determine the optimal dosage of rejuvenator, the rejuvenation index (*RI*), defined in Equation (3), was employed referring to previous works (Cavalli *et al.* 2018, Lin *et al.* 2021). Ageing mainly has a negative effect on the low-temperature performance of bitumen (Lin *et al.* 2021, Hu *et al.* 2023), therefore, the boundaries of the integration were set as 0 and 4 respectively to target the complex modulus (*G**) values generally found at low temperatures (high frequencies, *ξ*). Figure 3 illustrates the physical definition of the rejuvenation index. The rejuvenation index was defined as the ratio of the integration areas of rejuvenated and virgin bitumen. Therefore, it equals to the sum of blue and yellow shadowed areas divided by the yellow shadowed area.

$$RI = \frac{\int_0^4 \log|G*_{aged/rejuvenated}|\xi d\xi}{\int_0^4 \log|G*_{virgin}|\xi d\xi} \tag{3}$$

Mathematically, *RI* values greater than one indicate that the bitumen is aged or insufficiently rejuvenated, while on the contrary, *RI* values less than one suggest over-rejuvenation. Therefore, the closer *RI* to one, the better the rejuvenation effectiveness. The values of *RI* for the aged and rejuvenated binders with dosages of 3%, 4% and 5% of rejuvenator (for the first ageing-rejuvenating cycle) were 1.14, 1.03, 1.00, 0.99

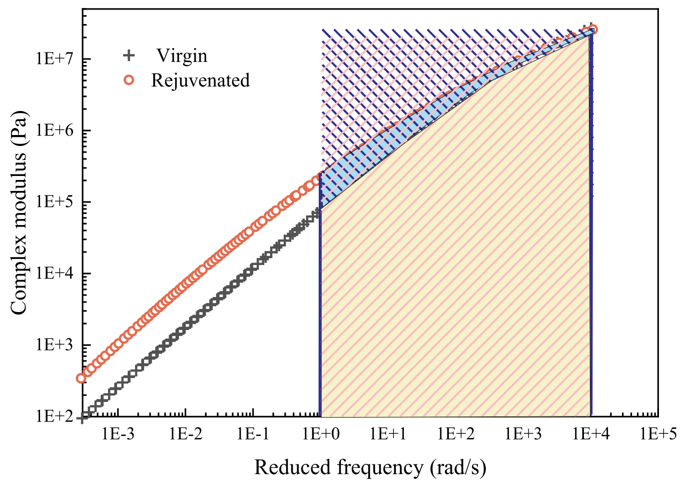


Figure 3. Schematic of rejuvenation index.

respectively, suggesting that 4% was the optimal dosage. On this basis, the bulk supply of the aged bitumen was blended with 4% of the rejuvenator. This rejuvenated bitumen was then subjected the same ageing protocol to produce re-aged bitumen, referred to as '2A-R'. This re-aged bitumen was then re-rejuvenated following the same protocol as described above until the fourth cycle of ageing and rejuvenation.

3.2.3. Rheology testing and performance evaluation

Based on the master curves, the complex modulus and phase angle of interest at any temperature and frequency can be computed. Previous studies suggested that the G-R parameter (Rowe *et al.* 2014) of bituminous materials matches well with the field durability performance of asphalt pavements (Makowska *et al.* 2017, Ogbo *et al.* 2019). Therefore, this parameter was employed in this study. The calculation for the G-R parameters (at 15°C and 0.005 rad/s) is shown in Equation (4).

$$G - R = \frac{G^*(\cos\delta)^2}{\sin\delta} \tag{4}$$

The linear amplitude sweep (LAS) tests were carried out at 25°C as per AASHTO T391-20 (AASHTO 2020). Firstly, a frequency sweep at 0.1% strain over a range of frequencies from 0.2-30 Hz was performed. Subsequently, a 'step' 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% to 30% with an increase of 1% strain per ramp.

The low-temperature DSR testing using 4 mm parallel plates with a gap of 2.2 mm was performed for a frequency sweep test at frequencies of 0.03, 0.1, 0.3, 1, 1.6, 3, 5, 8, 10, 20, and 40 Hz with temperatures of 0, −6, −12, −18, −24 and −30°C (Komaragiri *et al.* 2022, Hofer *et al.* 2023).

3.2.4. Testing on the generic fractions of bitumen

The generic polarity-based fractions of bitumen were detected using thin-layer chromatography with flame ionization detection (TLC-FID) (Lu and Isacsson 2002). The principle of this test was based on separating the fractions of bitumen according to their solubility in dedicated solvents. The saturates were separated firstly due to its good solubility in n-heptane and weak strength of interaction with the adsorbent, then aromatics and resins were separated using other solvents. Finally, the most polar and insoluble asphaltenes were left on the chroma rods.

4. Results and discussions

4.1. Rejuvenation index

As detailed in Equation (3), the rejuvenation indices for each ageing-rejuvenation cycle were calculated, as shown in Figure 4.

The rejuvenation index was used to determine the optimal rejuvenator dosages for repeated rejuvenation cycles. The results in Figure 4 show an optimal dosage of 4% for the first two cycles and 3% for the last two cycles. The *RIs* for the repeatedly aged binders (Aged, 2A1R, 3A2R and 4A3R) decreased with increasing ageing cycles, indicating that less and less rejuvenator was needed for the multiple cycles of rejuvenation. In other words, the rheological properties tended to be more stable after multiple cycles of ageing and rejuvenation. Since the high-temperature performance of bitumen always improves with ageing, there is less concern about the high-temperature performance in terms of repetitive ageing. This observation is consistent with previous studies, which used very soft bitumen (650/900 penetration grade) as their rejuvenator and a metric of penetration and G-R parameter of virgin bitumen as the target index (Makowska *et al.* 2017) and found that for the further cycles of rejuvenation, less rejuvenator was required to meet the rejuvenation target. However, the study only evaluated the rejuvenation effectiveness using penetration and G-R parameter and failed to disclose the low-temperature, fatigue life and the chemistry of the repetitive aged and rejuvenated bitumen. Though the rejuvenation index suggested that for the third and fourth cycles of rejuvenation, less rejuvenator is needed with a calculated optimal dosage of 3%. To have a fair and consistent comparison for the changes in properties, 4% was chosen for the dosage for all rejuvenation cycles.

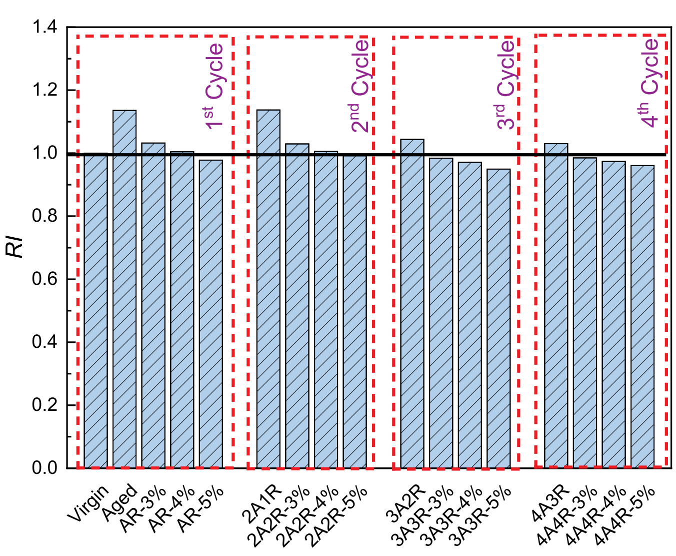


Figure 4. Rejuvenation index for binders after repetitions of ageing and rejuvenation.

4.2. Master curves of binders in terms of repeated ageing and rejuvenation

The complex modulus master curves of binders are shown in Figure 5.

For the first cycle, it was observed from Figure 5(a) that after ageing, the complex modulus of bitumen increased significantly. After rejuvenation, the binder was softened, and the complex modulus was reduced. However, the complex modulus master curves of the three rejuvenated binders at 3, 4 and 5% rejuvenator dosage relative to the complex modulus master curve of the virgin (unaged) binder are not consistent over the entire reduced frequency range. Within the low-frequency range (corresponding to high temperatures), the rejuvenated binders with 3% and 4% rejuvenator dosage had complex modulus values greater than those found for the virgin binder. At the high-frequency range (corresponding to low temperatures), the binders with varying dosages of rejuvenators were equivalent or slightly softer (lower complex modulus values) than the virgin binder and it can be assumed that rejuvenation had restored the aged binder to its virgin state with the rejuvenated binder with 4% dosage being optimal. At a dosage of 5%, the complex modulus master curve of the rejuvenated binder was seen to be higher than that for the virgin binder at the low frequency (high temperature) but below that at the high frequency (low temperature) conditions. This indicates that this aged binder was over-rejuvenated. For the following cycles, the trends were the same, with ageing increasing the complex modulus and rejuvenation decreasing it. Moreover, with increasing ageing-rejuvenation repetitions, the differences between the complex modulus master curves for the different dosages became smaller because the bitumen became less sensitive to ageing and rejuvenation. Figure 5(a) highlights the change to virgin binder behaviour after ageing with significantly increased G^* and reduction in the slope of the master curve, indicating reduced temperature susceptibility. Rejuvenation reduces G^* and shifts the slope of the master curve closer to that of the virgin binder.

In Cycle 2, as shown in Figure 5(b), ageing resulted in a lesser change in stiffness than in Cycle 1. The binder appeared to be more resistant to ageing related stiffening, becoming less stiff and viscous and retaining similar temperature dependence. With no change to the gradient, rejuvenation dosage in this cycle did not appear to change the stiffness-temperature relationship; instead, it only reduced G^* with each dosage, indicating the rejuvenator still successfully softened the binder. Cycles 3 and 4, as shown in Figure 5(c,d), portrayed the same patterns; Ageing increased stiffness and altered the temperature relationship less than in Cycle 1; Rejuvenation reduced complex modulus with higher dosages, whilst retaining the same modulus-frequency relationship as the aged binder in the cycle.

The master curves of complex modulus illustrate that an adequate dosage of rejuvenators can restore the stiffness of bitumen at high frequency range, however, the change in the stiffness of bitumen at low frequency range with the presence of rejuvenators is much less significant. In other words, the rejuvenation is more effective the lower-temperature performance of bitumen, previous literatures reported the similar trend (Karki and Zhou 2016, Hugener *et al.* 2022). This observation suggests that estimating the dosage of rejuvenators

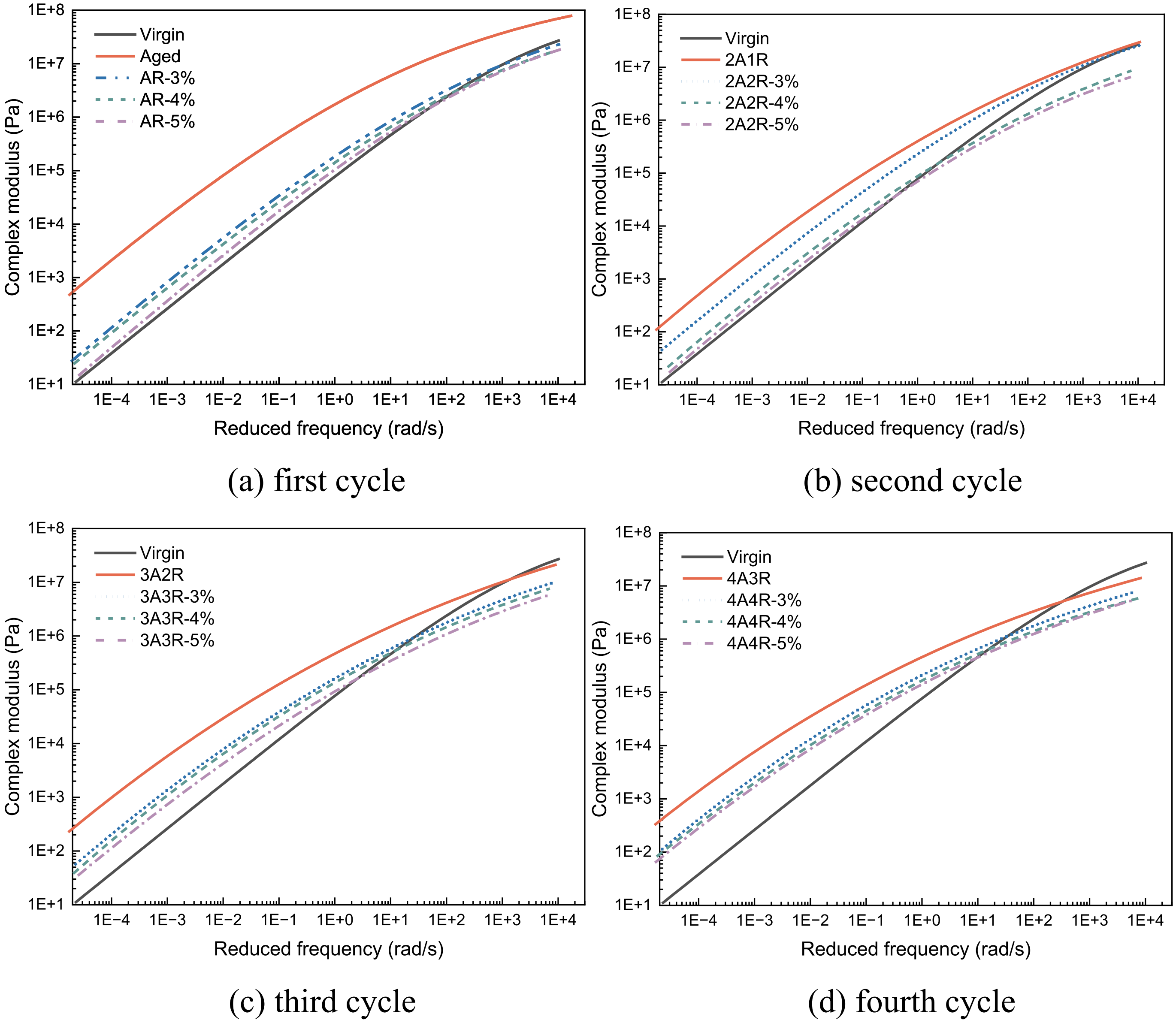


Figure 5. Master curves of complex modulus of binders with different dosages of rejuvenator.

based on just one rheological parameter does not necessarily mean that the expected change will°Ccur in other parameters. Therefore, the target based on conventional indices such as penetration, viscosity or ductility has obvious disadvantages (Lin *et al.* 2021, Zahoor *et al.* 2021, Hugener *et al.* 2022).

4.3. Black space diagram

The black space diagram represents rheological data of bitumen in the form of complex modulus against phase angle, without any shifting of the raw data (Airey 1997). Conveniently, the black space diagrams were commonly used to identify the testing geometry compliance errors. Recently, more advanced analysis techniques were proposed, like providing comprehensive understanding of the cracking susceptibility, durability, healing, etc (Airey *et al.* 2022). One of the useful applications of black space is integrating the G-R parameter to the black space diagram to have a visible view of the cracking resistance of bituminous binders. In accordance with the proposed criterion, the value equals to 180 kPa is corresponding to the damage onset, or cracking warning limit, while 450 kPa indicates significant cracking (Rowe *et al.* 2014). The black space diagram for binders after each cycle of ageing and rejuvenation (with 4% rejuvenators) is shown in Figure 6, with G-R parameter integrated.

The blue diamond in Figure 6 represents the virgin binder, the red circular points represent binders after each cycle of ageing, and the half-filled green pentagonal points represent binders rejuvenated with 4% of rejuvenators. The lines connecting virgin/rejuvenated and aged binders indicate the ageing history for every cycle. Firstly, it was observed that at this specific temperature (15°C) and frequency (0.005 rad/s), ageing makes the binders more brittle (higher complex modulus and lower phase angle), while rejuvenation recovers these changes. Specifically, the rejuvenation target employed in this study is complex modulus based, leading to the

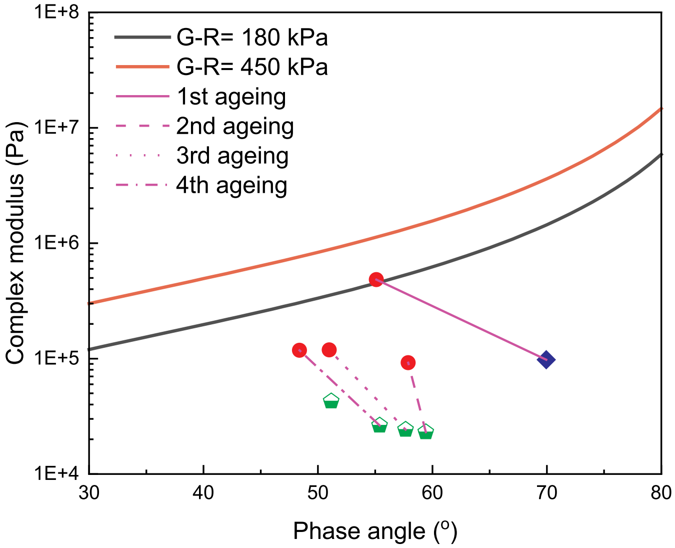


Figure 6. Black space diagram of virgin, aged and rejuvenated bitumen.

insufficient recovery of viscoelastic balance, which has similar results as stated in previous research (Makowska *et al.* 2017). Theoretically adding very high dosages of rejuvenators can make the phase angle recover to the level of the virgin binder, however, the bitumen would be quite soft and lose its physical properties (Zahoor *et al.* 2021). Therefore, the viscoelastic balance of bitumen is not a practicable target for rejuvenation. Table 1 elaborates the changes associated with G-R parameters in terms of ageing and rejuvenation cycles.

Table 1 shows that the G-R parameters of binder increases after each cycle of ageing, indicating the binders are getting more susceptible to cracking while rejuvenation reduces this susceptibility effectively. Notably, after the first cycle of ageing, the G-R parameter of aged binder exceeds 180 kPa, suggesting the initiation of cracking. However, for the following ageing cycles, although the G-R parameters of re-aged binders increase continuously, the amplitude is not that high. One of the possible reasons to explain this observation is the dual roles of rejuvenators – it plays the roles of both rejuvenator and antioxidant (Haghshenas *et al.* 2021). Another possibility is that the bitumen gets less and less sensitive to oxidation with the extension of ageing (Tauste *et al.* 2018). Nevertheless, the results illustrate that the growth rate of G-R parameters of binder after multiple cycles of rejuvenation is prolonged, suggesting the possibility of circular asphalt binders under this specific rejuvenation criteria, in terms of ductility and cracking resistance performance.

Table 1. G-R parameters for binder with varying ageing and rejuvenation cycles.

Cycle	Binder status	G-R parameter (kPa)
Virgin	V	12.2
1st cycle of ageing and rejuvenation	A	193.0
	AR	6.9
2nd cycle of ageing and rejuvenation	2A1R	30.8
	2A2R	8.1
3rd cycle of ageing and rejuvenation	3A2R	60.7
	3A3R	10.3
4th cycle of ageing and rejuvenation	4A3R	69.6
	4A4R	21.5

4.4. Intermediate-temperature performance evaluation

In the previous version of the linear amplitude sweep (LAS) standard (AASHTO TP101-14), the peak in stress was defined as the damage failure point in terms of fatigue characterisation. Though the updated AASHTO T391-20 discarded this criterion and employed the 35% reduction in $G^{*}sin\ \delta$ as the damage criterion, the stress–strain curves, as shown in Figure 7 could still be regarded as an effective approach to have an insight into the failure properties of bituminous materials.

In the first cycle of ageing and rejuvenation, it was observed that the stress of the aged binder reached the peak earlier than other binders, suggesting that ageing reduced the damage tolerance of binders as expected. After rejuvenation, an increase in 'strain at peak stress' was observed with higher dosages always associated with a larger value of strain at peak stress, indicating that rejuvenated binders can endure larger strains. The trends for the second, third and fourth cycles were the same. During the following cycles, the re-aged binders endured even larger strain compared to the virgin binder and the higher dosages showed better damage tolerance. Comparing the stress–strain curves of each cycle of ageing and each cycle of rejuvenation with the defined 'optimal' dosage of 4% shows that more cycles of ageing significantly improved the damage tolerance of binders, leading to the reduction in stress as seen in Figure 7(e,f) respectively. The same trend was observed for the multiple cycles of rejuvenation, with rejuvenated binders having even better performance than virgin binder.

The AASHTO standard recommended utilising 2.5% and 5% as the strain levels to evaluate the fatigue life of bituminous materials. However, recent publications pointed out that the fatigue life of binders at low strain levels has a poor correlation with the fatigue performance of asphalt mixtures, and therefore higher strain levels, for example, exceeding 10%, will be a better alternative (Chen and Bahia 2021). Given that, this study employed six strains, which were 2.5%, 5%, 7.5%, 10%, 12.5% and 15% to calculate the fatigue life of bitumen at all ageing or rejuvenation conditions. The fatigue lives obtained from the lowest and highest strain levels are shown in Figure 8.

As shown in Figure 8, at 2.5% strain, ageing increased fatigue life and rejuvenation reduced it, however at 15% strain, it shows opposite results. The improved fatigue life after ageing at low strains is due to the hardening of the binder which at low stress and strain levels results in greater fatigue lives (Chen and Bahia 2021). The fatigue life of binders at high strains was reported to have a strong correlation with that of asphalt mixtures and therefore the fatigue life at 15% strain is more relevant (Chen and Bahia 2021). Increasing the rejuvenator dosages extended the fatigue life of binders for all cycles. Moreover, ageing reduced the fatigue life of binders since the values of all re-aged binders were lower than that of the previous rejuvenated binder with 4% of rejuvenator. It's also notable that after the repetitions, the fatigue life of binders increases with repeated cycles. The strain dependency or sensitivity of the fatigue lives of binders is shown in Figure 9.

It was observed from Figure 9 that for the first cycle of ageing, the fatigue life of bitumen increased when the strains were

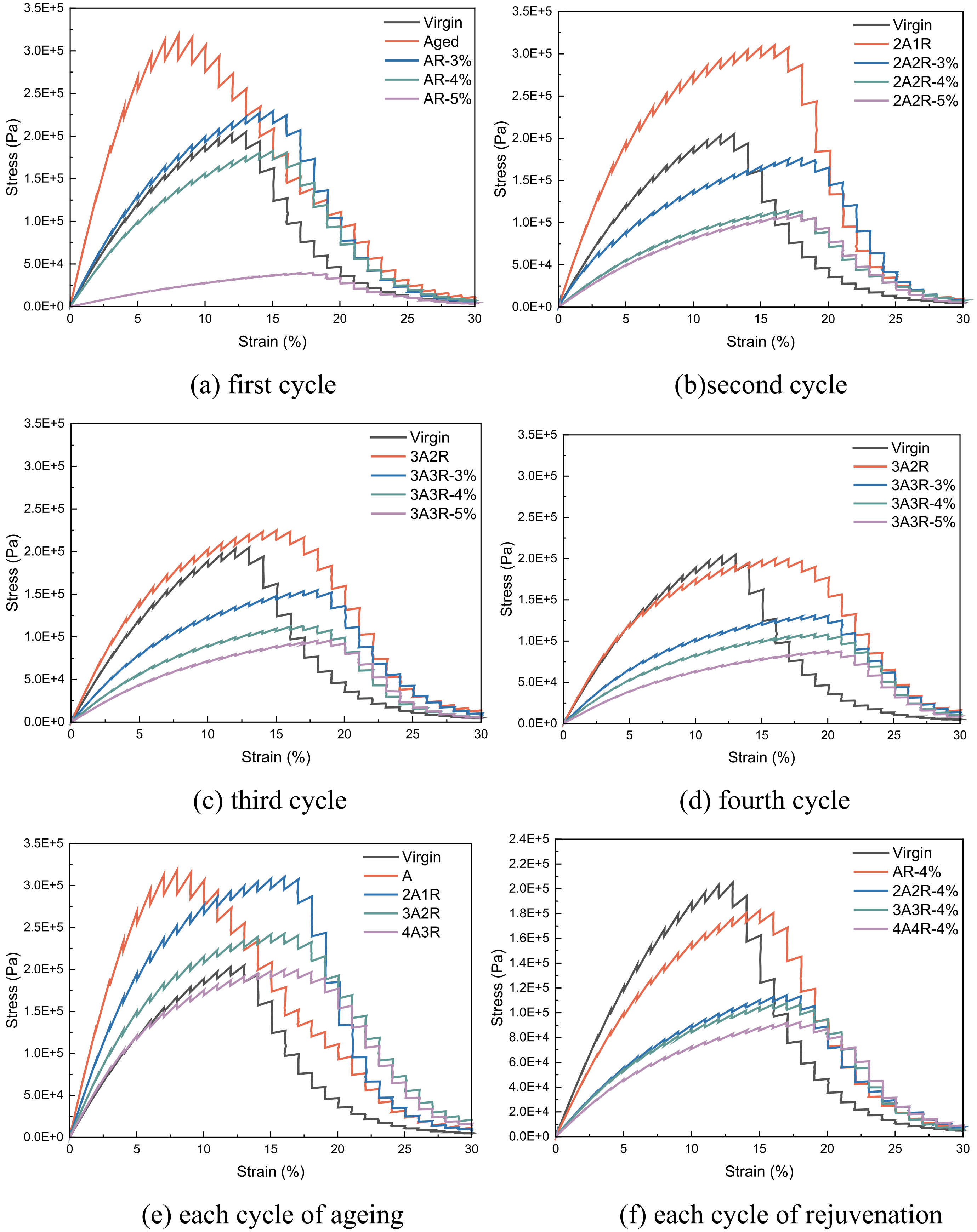
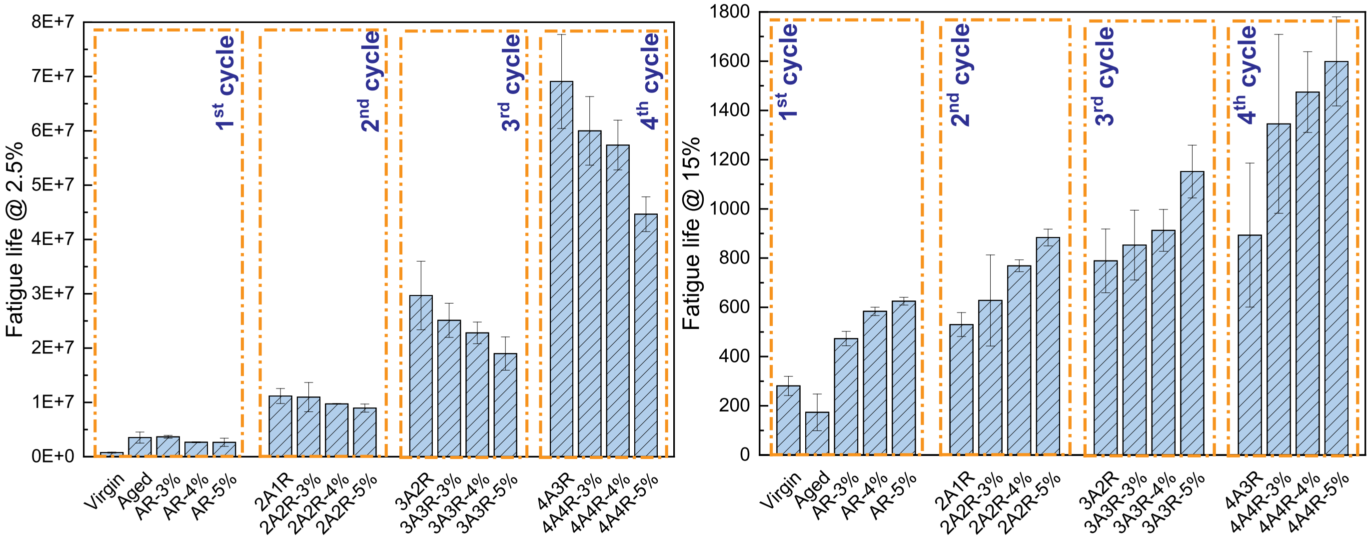


Figure 7. Stress-strain curves of bitumen after repetitions of ageing and rejuvenation.



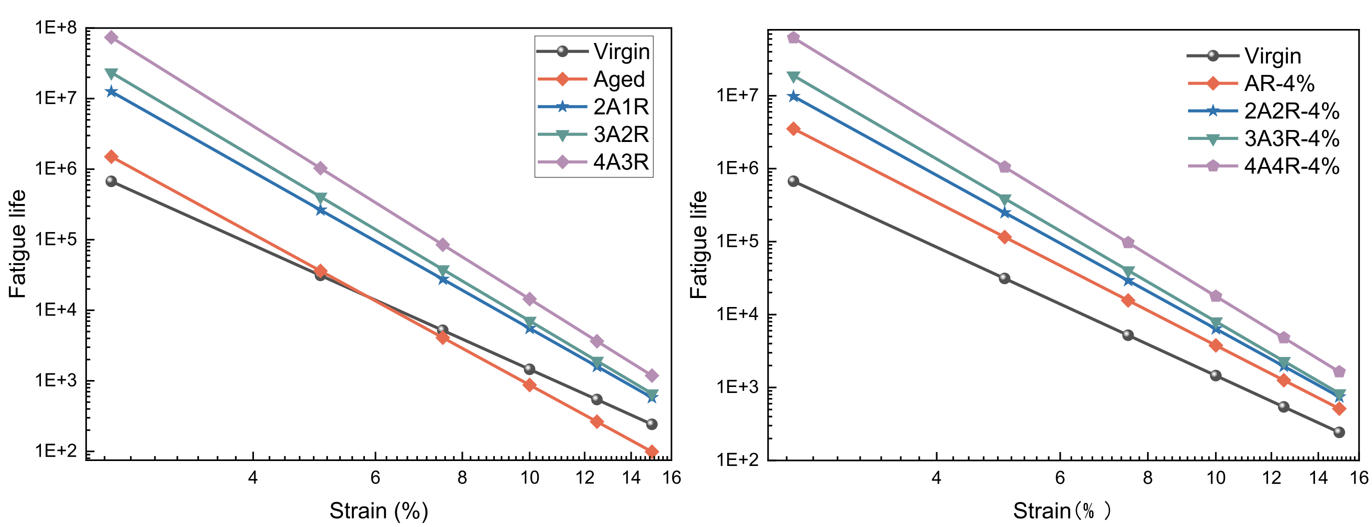
(a) strain equals to 2.5% (b) strain equals to 15%

Figure 8. Fatigue life of bitumen.

relatively low, while decreasing at high strains. For the following cycles, repeated ageing resulted in a continuous increase of fatigue life compared to the last cycle of ageing, regardless of the strain levels. It is noteworthy that the slopes of the curves increased continuously with ageing cycles, denoting that those increased repetitions of ageing made bitumen more sensitive to strain. The same trend was observed for repeated rejuvenation. The fatigue performance of bitumen in terms of repeated ageing and rejuvenation showed enhanced fatigue resistance in binders subjected to rejuvenation, although with an increased sensitivity to strain. It should be emphasised that this finding is based on using the same dosage of rejuvenator for each cycle, which made the re-rejuvenated bitumen softer than the virgin binders at low temperatures. Nevertheless, the results suggested that the fatigue resistance of repetitive ageing and rejuvenation can be assured after multiple cycles of rejuvenation.

4.5. Low-temperature performance evaluation

The most commonly used equipment used for low-temperature performance evaluation of bitumen is the bending beam rheometer (BBR). However, its application for evaluating the low-temperature properties of recycled binders is laborious due to a large amount of material required for the test. To overcome this, studies have explored the option of using the 4-mm DSR as an alternative to the BBR. In accordance with the literature, this study adopted the most recently proposed approach, which dictates a direct cut-off value for G^* equal to 160 MPa and phase angle equal to 25° at the frequency of



(a) repetition of ageing (b) repetition of rejuvenation

Figure 9. Relationships between fatigue life of binders and strain.

0.2 rad/s (Komaragiri *et al.* 2022) to examine the low-temperature performance of bitumen. The results of repetitions of ageing and rejuvenation of the binders rejuvenated by 4% of rejuvenator are summarised in Table 2. It should be noted that due to the limitations of the rheometer, the lowest temperature was −30°C, however, at this temperature, some binders still met the metric of the predefined cut-off value. Given that, the results at −36°C and −42°C were predicted based on the time-temperature superposition principle. Firstly, master curves of the binders were built following the modified CAM model at −36°C and −42°C, using Equations (1) and (2). Since the complex modulus and phase angle master curves are functions of reduced frequency, the values at 0.2 rad/s can easily be calculated and used to calculate the critical temperatures of the aged and rejuvenated binders.

It was observed from Table 2 that after ageing, the low PG of binders reduced two grades from −28°C to −16°C. However, rejuvenation reversed this trend, improving the low PG of the binders. In addition to the low PG, the critical temperatures are also widely used to denote the cracking susceptibility of bitumen at low temperatures. The critical temperatures were calculated by the approach used by Anderson et al. (Anderson *et al.* 2011). In this study, the stiffness and m-value were replaced by complex modulus and phase angle respectively. The complex modulus greater than 160 MPa and the phase angle less than 25° was defined as failure (Komaragiri *et al.* 2022).

It can be observed from Table 2 that ageing led to more negative critical temperatures (suggesting increased susceptibility to thermal cracking) while rejuvenation always reversed this trend. It was found that after each cycle of ageing, the critical temperatures for both stiffness and creep rate decreased compared to last cycles, indicating that repeated ageing did not necessarily reduce the low-temperature performance of bitumen if it was appropriately rejuvenated before the next cycles of ageing. It should be noted that the ageing process itself is detrimental to the thermal cracking resistance of binders (Abdelaziz *et al.* 2020, Zhang *et al.* 2021). In that sense, the reason behind the improvement of low-temperature performance was exclusively the repeated rejuvenation process. Overall, the results suggest that after multiple cycles of ageing and rejuvenation, the usability of bitumen is still tenable. Particular attention should be paid in terms of overdosing since the low-temperature performance of the rejuvenated binders were better than the virgin binder. However, the evidence from this study suggests that if sufficient rejuvenator is added, the critical temperatures and the same low PG of bitumen can be recovered after multiple cycles of rejuvenation.

Table 2. Low-temperature properties for binders after repeated ageing and rejuvenation.

Binder code	Lower PG	Critical temperatures (°C)		ΔTc
		$T_{C,S}$	$T_{C,m}$	
V	−28	−29.69	−28.27	−1.4
A	−16	−26.58	−21.08	−5.5
AR	−34	−38.90	−34.30	−4.6
2A1R	−28	−35.04	−28.65	−6.4
2A2R	−40	−46.43	−41.78	−4.7
3A2R	−28	−41.63	−28.14	−13.5
3A3R	−40	−52.98	−41.63	−11.3
4A3R	−22	−45.88	−27.25	−18.6
4A4R	−40	−52.98	−41.63	−11.4

In addition to the critical temperatures, another parameter, ΔTc, defined as the difference between these two critical temperatures, can also be employed to examine the low-temperature performance of bituminous materials. The rise in interest of whether the performance grade of bitumen is governed by its stiffness or creep rate has facilitated the popularity of the utilisation of ΔTc. It is understood that if the value of ΔTc is positive, the PG is stiffness controlled and if the value is negative, then the PG is creep rate controlled (Asphalt Institute 2019). Additionally, it has been documented that ageing will lead to more negative values of ΔTc (Asphalt Institute 2019). The results in this paper showed consistent trends with literature results, the ΔTc was −5.4°C for the first cycle of ageing and −18.6°C for the fourth cycle of ageing, indicating that more cycles of ageing led to more negative value of ΔTc. The ΔTc being lower than −5°C usually indicates that the binders are very susceptible to cracking. For the repetitions of rejuvenation, it was found that every rejuvenation cycle recovered the ΔTc to a small extent. However, the ΔTc still became more negative with the increasing cycles of rejuvenation, which might suggest that the binders might be very susceptible to cracking after multiple cycles of rejuvenation (Makowska *et al.* 2017, Koudelka *et al.* 2019). Therefore, the m-value of bitumen after multiple cycles of ageing and rejuvenation could be a slight concern which might limit the repeated reuse of aged bitumen.

The results show that the repetitions of ageing and rejuvenation did not necessarily reduce the low-temperature performance of bitumen, on the contrary, repeated rejuvenation might result in lower critical temperatures, which indicates better thermal cracking resistance. However, the repeated ageing resulted in significant alteration in the ΔTc (more negative), which might be associated with high susceptibility to cracking. It's noteworthy that at the case of very negative ΔTc, the critical temperatures were extremely low while the ambient temperature might be much higher than the critical temperatures of bitumen. Therefore, the binders will likely perform work well without the need to consider the ΔTc. However, further analysis is required to investigate this.

4.6. Chemical fractions of bitumen under repetitive ageing and rejuvenation

Due to the complexity of the chemistry of bitumen, it is not feasible to separate bitumen into individual components that make up its colloidal structure. One of the standard practices is separating bitumen into its polarity based fractions i.e. saturates, aromatics, resins, and asphaltenes, which is commonly termed as SARA fractionation (Corbett 1969). The ageing of bitumen has a significant influence on the chemistry of bitumen including SARA fractions. It is well recognised that ageing leads to a significant reduction in the content of aromatics while an increase in the contents of resins and asphaltenes. Saturates are considered inert to ageing, consequently, the content of saturates remains relatively stable during ageing (Loeber *et al.* 1998, Lu and Isacsson 2002, Lesueur 2009). Rejuvenation, however, can theoretically rebalance the changes in the chemistry of bitumen during ageing (Yu *et al.* 2014). The generic fractions of bitumen were measured, as shown in Figure 10.

From Figure 10, it can be seen that ageing led to the very slight decrease in the content of saturates, significant decrease in the content of aromatics, significant increase in the contents of resins and asphaltenes, which is consistent with previous research efforts (Loeber *et al.* 1998, Haghshenas *et al.* 2022). In terms of rejuvenation, it was found that upon the introduction of the rejuvenator used in this study, the most significant increase occurred with the content of resins, accompanied by a slight increase in the contents of saturates and aromatics. This illustrates that the main component of this rejuvenator might be resin-like, which led the increase of the content of resins. This observation was consistent with all ageing and rejuvenation cycles.

In summary, ageing and rejuvenation had very limited influence on the content of saturates, only slight fluctuations were observed, this observation has been well documented through evaluation by both the TLC-FID separation approach and solid phase extraction (SPE) approach (Lu and Isacsson 2002, Mirwald *et al.* 2020b). In terms of the content of aromatics, ageing led to its content to significantly decrease while rejuvenation led to its slight recovery (Osmari *et al.* 2017). Therefore, with multiple cycles of ageing and rejuvenation, the content of aromatics tended to decrease. When considering the content of resins, both ageing and rejuvenation led to significant increases. Therefore, after four cycles of ageing and rejuvenation, the content of resins doubled. Finally, ageing led to a rise in the content of asphaltenes while rejuvenation can counteract this increase. Therefore, after multiple cycles of ageing and rejuvenation, the content of asphaltenes can remain mostly balanced. It should be noted that the contents of SARA fractions are relative values instead of absolute values. The decrease in the content of asphaltenes might be caused by the supplementation of light fractions, which reduced the relative content of asphaltenes. Therefore, the reduction in the content of asphaltenes does not necessarily imply the asphaltenes can be dissolved or dispersed by means of rejuvenation (Osmari *et al.* 2017). The colloidal index, which is widely used to identify the chemical stability of bitumen (Loeber *et al.* 1998), was employed in this study. The colloidal index can be calculated using Equation (5). The results are shown in Figure 11.

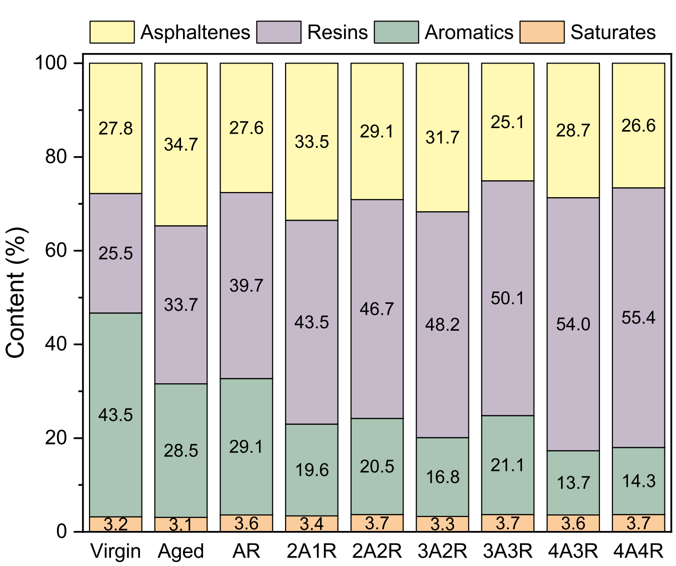


Figure 10. Generic fractions of binders.

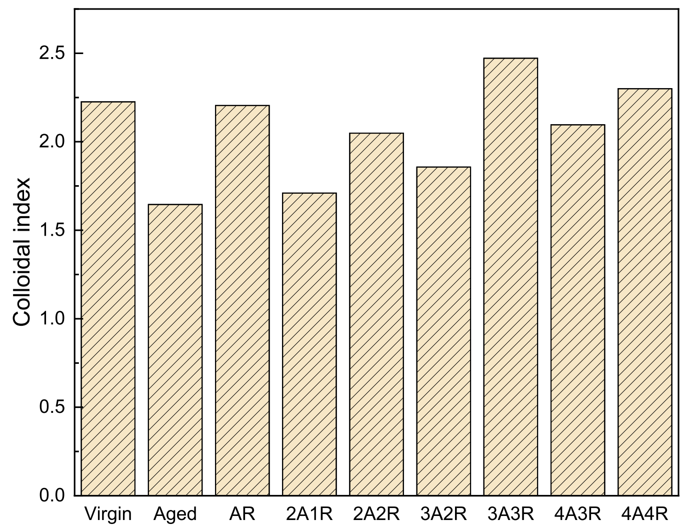


Figure 11. Colloidal indices of binders after multiple cycles of ageing and rejuvenation.

$$CI = \frac{Aromatics + Resins}{Saturates + Asphaltenes} \tag{5}$$

It can be seen from Figure 11 that after ageing, the colloidal index of bitumen decreased, which is reported to lead to a less chemically stable binder, and results in increased cracking susceptibility (Lesueur 2009). However, the results indicate that rejuvenation cycles can reverse the deterioration of the chemical stability by increasing the content of resins and decreasing the content of asphaltenes. Therefore, regardless of the recycling cycles, the colloidal index of rejuvenated bitumen could be recovered to its initial level. This result supports the rheological data observed in this study and indicates why the rheological performance of bitumen can always be recovered after rejuvenation. Unfortunately, the SARA analysis only provides a superficial understanding of the chemical changes within bitumen in terms of multiple ageing and rejuvenation cycles. The microchemistry and mechanisms of rejuvenation needs to be further elucidated through more advanced chemical investigations.

5. Conclusions

This study evaluated the properties of bitumen after multiple cycles of ageing and rejuvenation to explore the feasibility and challenges of manufacturing fully recycled binders for circular pavement construction. The low-temperature and intermediate-temperature (fatigue) rheology was comprehensively evaluated to illustrate the changes upon repetitive recycling. Moreover, polarity-based fractionation using SARA analysis was carried out to further understand the trends observed in chemical changes. Based on the results, the following conclusions can be drawn.

(1) This study employed a master curve-based rejuvenation index to calculate the optimal rejuvenator dosage for each rejuvenation cycle. The optimal dosage for repeated recycling shows a decreasing tendency, which indicates that as cycles of rejuvenation increase, less rejuvenator is likely needed to meet performance requirements.
(2) Upon adding the appropriate dosage of rejuvenator, the fatigue life and lower PG of repeatedly rejuvenated bitumen can be maintained. Though the G-R parameter of repeatedly rejuvenated bitumen showed an increasing trend, implying that the binders would be more susceptible to cracking, the growing rate observed was very slow.
(3) The most concerning result was related to the delta *Tc* parameter. For every cycle of rejuvenation, the critical temperatures can be recovered to a comparable level to that of a virgin binder. However, after two cycles of ageing and rejuvenation, the delta *Tc* would be very negative, suggesting the potential strong susceptibility to thermal cracking. The ramification of this result needs further deliberation in upcoming studies.
(4) Based on the rejuvenation indices, it was implied that after repeated recycling, the ageing resistance of binder gets better. There are two possible reasons: (1) With more cycles of ageing, the binder gets stiffer and more elastic, and its physicochemical properties tend to be relatively stable, as previous study efforts stated that the properties of bitumen changes very slightly after 80 hours of PAV ageing; and (2) The rejuvenator plays a dual role in the process, both as rejuvenator and anti-ageing agent.
(5) In terms of chemical fractions, the trend is consistent for multiple cycles of ageing and rejuvenation. Both ageing and rejuvenation have very limited influence on the content of saturates, while both increases the content of resins significantly. Ageing also leads to a decrease in the content of aromatics and an increase in the content of asphaltenes while rejuvenation has the opposite impact on these two fractions. Ageing can reduce the chemical or colloidal stability of bitumen while rejuvenation can recover this property to initial level.

Overall, this study comprehensively investigated the feasibility of repetitive recycling of aged bitumen for more circular asphalt pavement construction. A limitation associated with this study is that only one dosage optimisation metric and one bitumen and rejuvenator were used. For further study, it is recommended to employ varying metrics to evaluate the rejuvenation efficiency after multiple cycles of ageing and rejuvenation. Moreover, it is also recommended to use different types of bitumen and rejuvenators to study the potential effect of material dependency. Lastly, recycling is unlikely to be 100% in most cases and virgin bitumen would be required to be blended with the rejuvenated mixtures. This could lead to potential compatibility issues between them. Therefore, it is recommended to investigate the compatibility between virgin and rejuvenated bitumen, especially after multiple cycles of aging and rejuvenation with large content of rejuvenators being introduced. One of the possible methods for this investigation would be using Hassen Solubility Parameter (HSP) approach (Sreeram *et al.* 2019, Sreeram *et al.* 2020).

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