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Rheological and chemical evaluation of aging in 100% reclaimed asphalt mixtures containing rejuvenators

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ABSTRACT

Rejuvenators improve the performance of reclaimed asphalt mixtures but relatively little is known about their long-term aging characteristics. This study evaluated the effect of four different rejuvenators on aging characteristics of 100% reclaimed asphalt mixtures. Rheological tests on extracted bitumen revealed that tall oil-based rejuvenator showed highest reduction and petroleum-based rejuvenator showed lowest reduction in stiffness of binder in the long term. At lower strain levels, the fatigue life calculated from linear amplitude sweep test was significantly higher for long-term aged binder compared to unaged binder due to increase in stiffness of bitumen. All the rejuvenated binders showed rutting performance comparable to that to virgin binder. Fourier transform infrared spectroscopy showed increased carbonyl peak intensity after long-term aging, but no clear implications were made for effect of aging on sulfonyl index.

1. Introduction

Recycling of asphalt pavements have received much attention in the recent years due to environmental concerns and increasing cost of raw materials used for pavement construction. In the United States, the test sections have successfully demonstrated the use of up to 30% of reclaimed asphalt in the pavement mixtures without compromising the performance as compared to conventional mixtures [1,2]. In laboratory, some of the studies have shown that asphalt mixtures containing 100% RA material provide satisfactory performance [3–6]. However, the concept of 100% recycling, where the asphalt mixture is produced using only reclaimed asphalt, bitumen, and rejuvenators, needs validation through more studies. Most of the laboratory studies have used either a softer binder, an additive, or a rejuvenator to modify the reclaimed asphalt (RA) binder. Among these, rejuvenators are most effective in adjusting the properties of the RA binder and improving the performance of final mixtures. Rejuvenators can be petroleum based, bio oil-based, waste cooking or industrial oil based, or specifically engineered additives [7], and these rejuvenators can restore the asphaltenes/maltenes ratio in bitumen which compensates the hardening effect of aged binder [8,9]. However, rejuvenators from various sources may have different degree of effectiveness on improving the performance of the mixtures [10]. For example, the organic based rejuvenators have outperformed the petroleum-based rejuvenators in improving the performance of reclaimed asphalt mixtures [11]. Another study found that rejuvenators based on paraffinic oil were less effective in improving fatigue life of mixtures compared to fatty acids-based rejuvenators [12]. Though significant work has been conducted on understanding the effect of rejuvenators on RA binder properties [13–17], relatively little is known about the long-term effectiveness of these rejuvenators and their interaction with asphalt binder during pavement aging.

The oxidation of bitumen is the main reason behind deterioration of pavement during service life and as a result, pavement becomes more susceptible to thermal cracking and fatigue failure. The aging of asphalt mixtures is divided into two main stages: short-term aging, which is due to volatilization of the bitumen within the asphalt mixture during mixing and construction, and long-term aging, which is due to oxidation and steric hardening in the field [18]. The researchers have made efforts to simulate the field aging in the laboratory at both binder and mixture level. Rolling thin film oven test (RTFOT) and Pressure aging vessel (PAV) are the most frequently used methods on binder for short-term and long-term aging, respectively [19–22]. However, the aging

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procedures on binder aging do not completely simulate the field conditions because aging depends on binder as well as on mix parameters [23]. The long-term aging of bitumen in field is a slow process and depends on a number of environmental factors. Therefore, aging methods that consider the impact of reactive oxygen species have been developed to simulate the field aging [24,25]. This method leads to different aging level which makes it more suitable to distinguish between aging susceptibility of different binders [26]. Even after considering the environmental factors, the aging in mixture differs from binder aging. For examples, it was shown that degree of aging was found to be spatially dependent which resulted in stiffness gradient within the asphalt layer [27]. Therefore, several studies have investigated the effect of short-term oven aging [28,29] and long-term oven aging [30,31] on properties of asphalt mixtures containing RA material. It has to be noted, however, that the maximum RA content in asphalt mixture is limited to 50% or less in most of the studies. In the past, reclaimed asphalt has shown a slower aging rate compared to a virgin binder [32,33]. Therefore, it becomes important to study the aging of binder in 100% RA mixtures, as these mixtures may contain high amount of inactive RA binder along with rejuvenated binder which may age at a different rate. Moreover, with a wide variety of rejuvenators available in the market, it is likely that the type of rejuvenator used in the mixture will also affect its binder aging phenomenon. All these factors will affect the rate of aging of mixtures which needs to be investigated.

2. Objective

The objective of this study is to evaluate the change in rheological and chemical properties of bitumen by simulating the aging on 100% reclaimed asphalt mixtures containing different sources of rejuvenators. The experimental plan is shown in Fig. 1. The field aging simulation was conducted on loose mixtures in oven to consider the effect of varying aging rates of different stiffness of binder layers present in the RA material. The rheological characteristics were evaluated using temperature and frequency sweep test, fatigue performance was evaluated using linear amplitude sweep test, rutting performance was evaluated using multiple stress creep recovery test, and functional group characterization was performed using Fourier transform infrared spectroscopy.

3. Materials and methods

3.1. Materials

The reclaimed asphalt material was collected from an asphalt plant in Latvia. The collected RA material was fractionated to 10/22 size to remove the fines in order to meet the gradation criteria of AC-16 mixtures from Latvian road specifications. The gradation of original RA material and 100% RA mixtures (10/22 RA material) are shown in Fig. 2. The centrifuge extraction was performed on RA material according to EN 12697–1 [34] and the binder was recovered from the solution using a rotary evaporator according to EN 12697–3 [35]. The properties of RA material are given in Table 1. Four commonly used commercial recycling agents including one tall oil-based rejuvenator (R1), one vegetal oil and polymer-based rejuvenator (R2), one bio oil-based rejuvenator (R3), and one petroleum-based rejuvenator (R4) were used in this study shown in Fig. 3. The supplier recommended dosage for all the rejuvenators was approximately 5% w/b of RA binder and same was used for preparation of asphalt mixtures. The prominent functional group present in rejuvenators were identified from FTIR spectra using Bruker spectral interpretation library and are listed along with corresponding wavelength in Table 2. A distinct peak for rejuvenator has been observed in FTIR spectra of binders in the past studies [13,36,37]. In this study around 1740 cm^{-1} as shown in Fig. 4, the unique peaks were observed for three of the rejuvenators R1, R2, and R3, while it was absent for R4 (petroleum-based rejuvenator) as well as for virgin binder.

3.2. Sample preparation

For the preparation of asphalt mixtures, the RA material was heated at a temperature of 155 °C for 2.5 h. The heated RA material was transferred to the mixing bowl and the rejuvenator was added on RA material in the mixer, followed by mixing for 5 min. The loose mixtures were subjected to one of the three aging conditions – unaged (UN),

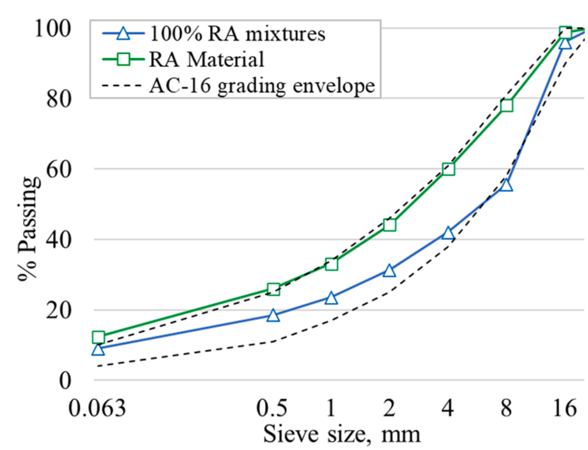


Fig. 2. Aggregate gradation.

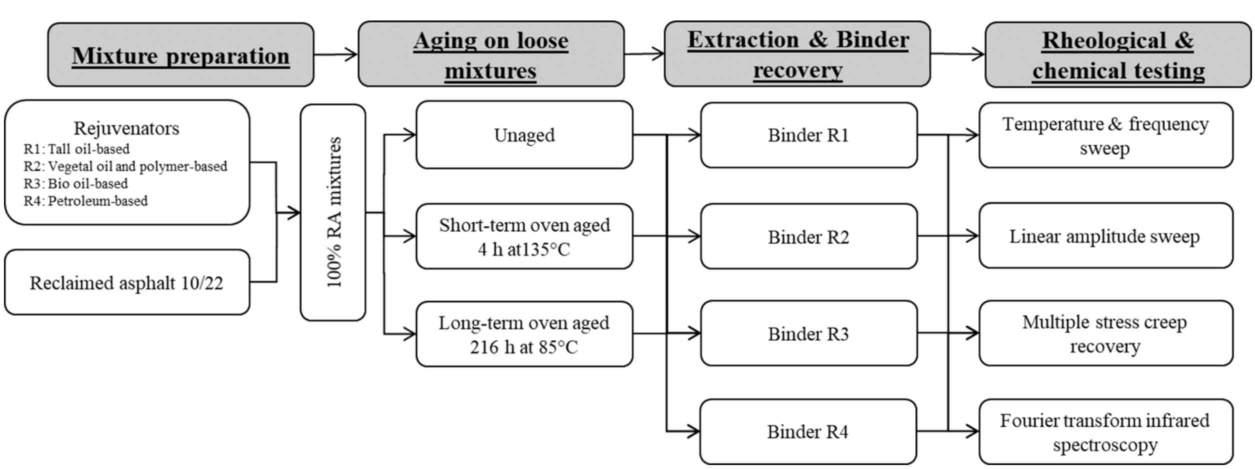


Fig. 1. Research plan.

Table 1
RA material characteristics.

Test method	Result	Standard
Binder content in RA material (%)	4.35	EN 12697–1 [34]
Flow coefficient of fine aggregates	28	EN 933–6 [38]
Shape Index of coarse aggregates	12	EN 933–4 [39]
Penetration of RA binder (0.1 mm)	39	(EN, 1426 [40]
Softening point of RA binder (°C)	58	(EN, 1427) [41]

short-term aged (STA), and long-term aged (LTA). The unaged mixtures were stored at room temperature following the mixing process. For simulating the short-term aging, the loose mixtures were conditioned at a temperature of 135 °C for 4 h according to SHRP-A-383 [42]. For simulating the long-term aging on mixtures, the loose mixtures were subjected to short-term aging, followed by conditioning at a temperature of 85 °C for 216 h according to RILEM recommendations [42]. Finally, binder was extracted from all the mixtures using toluene as solvent in centrifuge method and recovered from the solution using rotary evaporator. A total of 12 bitumen samples with different rejuvenators and aging conditions were obtained from mixtures. For reporting the results, the bitumen samples are identified based on their respective aging condition (VB- virgin bitumen, UN- unaged, STA- short-term aged, or LTA- long-term aged) and type of rejuvenator (R1, R2, R3, or R4).

3.3. *Test methods*

3.3.1. *Temperature and frequency sweep test*

This test was performed using a dynamic shear rheometer according to EN 14770. The bitumen samples were conditioned at 20 °C and were subjected to a set of 10 frequencies ranging from 0.1 Hz to 30 Hz. Following this, the temperature was raised with intervals of 10 °C up to 80 °C and a frequency sweep was performed at each test temperature. A

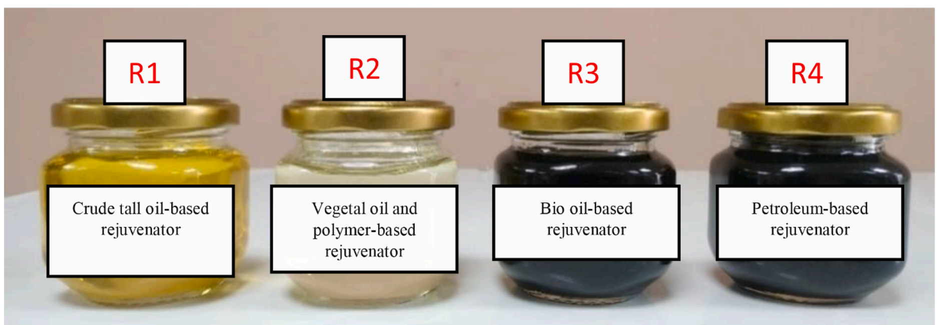


Fig. 3. Rejuvenators used in this study.

Table 2
Functional groups along with corresponding wavelength of absorption (in cm^{-1}) from FTIR spectrum analysis of rejuvenators.

	Aliphatic Propionate Esters	Olefins	Aliphatic hydrocarbon	Meta substituted aromatic hydrocarbons	Aliphatic Acetate Esters
R1	1750, 1200, 1100	3050, 1660	2890, 1450, 1375	×	×
R2	×	×	2915, 1450, 1375, 738	3050, 1900, 1600, 1500, 800	×
R3	×	3050, 1675	2925, 1463, 1375, 730	×	1750, 1250, 1065
R4	×	×	2915, 1463, 1375, 730	×	×

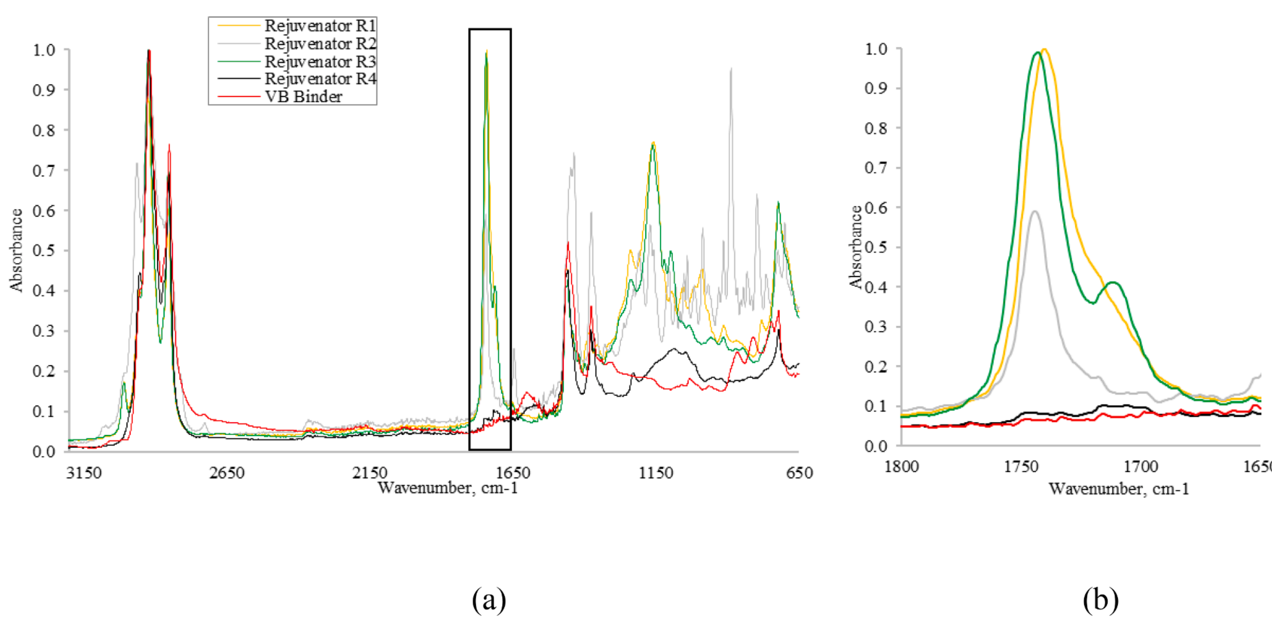


Fig. 4. Normalised FTIR spectra for all the rejuvenators used in this study between 900 and 1800 cm^{-1} wavelength. (a) Full spectra; (b) magnified area.

25 mm diameter spindle with 1 mm gap width was used under strain-controlled testing mode. The obtained data were shifted to the reference temperature of 20 °C using temperature – time superposition principle to prepare mastercurves of complex shear modulus (G*). The shift factors were calculated using Eq. (1) given by Williams et al., [43]. A sigmoidal function as defined by Eq. (2) was used for fitting the shifted data.

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \tag{1}$$

$$\log G^* = \delta + \frac{\alpha}{1 + e^{\beta + \gamma(\log a_T + \log g)}} \tag{2}$$

where a_T is shifting factor, C_1 and C_2 are material constants, and δ, α, β, γ are fitting parameters determined using the least squares method.

Dynamic shear rheometer is recommended by RILEM TC 252-CMB to capture the effects of aging on the binder [44]. Aging index have been used in the past studies to represent the effect of oxidation on bitumen [13,45]. In this study, to interpret the mastercurve results, two indices were defined, namely aging index (I_A) and softening index (I_S). The aging index indicates the increase in stiffness of bitumen as compared to the virgin bitumen. The softening index indicates the reduction of stiffness of bitumen as compared to the RA binder. Both of these indices are based on calculating the area under the mastercurve of given sample and a reference sample within a definite range of reduced frequencies as shown in Fig. 5. The reference sample for aging index is the virgin bitumen, and the reference sample for softening index is the RA binder. Eq. (3) and Eq. (4) were used to calculate the aging index (I_A) and softening index (I_S), respectively:

$$I_A = \frac{\int_{-5}^{-1} \log G^* df}{\int_{-5}^{-1} \log G^*_{VB} df} \tag{3}$$

$$I_S = \frac{\int_{-5}^{-1} \log G^*_{RA} df}{\int_{-5}^{-1} \log G^* df} \tag{4}$$

where, G* is complex modulus of binder for index calculation, f is logarithm of reduced frequency, G^*_{VB} and G^*_{RA}, are complex modulus of virgin bitumen and RA binder, respectively.

3.3.2. Linear amplitude sweep test

Linear amplitude sweep test was performed on dynamic shear rheometer according to AASHTO TP101 [46], to evaluate the fatigue characteristics of binder. The test is conducted in two stages using an 8 mm diameter spindle with a 2 mm gap width at a test temperature of 25 °C. In the first stage, the bitumen is subjected to a frequency sweep to determine a damage analysis parameter (α). A load of 0.1 percent strain is applied over a range of frequencies from 0.2 to 30 Hz. The second stage consists of oscillatory shear, in strain-controlled mode, at a frequency of 10 Hz. Strain is increased linearly from 0.1% to 30% over the course of 3100 cycles of loading, for a total test time of 310 s. Peak shear strain and peak shear stress are recorded every 10 load cycles (1 s), along with phase angle and complex shear modulus. The fatigue life (N_f) is calculated using a viscoelastic continuum damage (VECD) model according to Eq. (5).

$$N_f = A(\gamma)^{-B} \tag{5}$$

where A and B are VECD model coefficients, and γ is the strain amplitude.

3.3.3. Multiple stress creep recovery test

Multiple stress creep recovery test was performed on dynamic shear rheometer according to AASHTO TP70 [47], to evaluate the rutting characteristics of binder. The test was conducted in creep mode at 60 °C using a 25 mm diameter spindle with 1 mm gap width. The test procedure includes applying a series of static loads, followed by a recovery period, and measure the non-recoverable creep compliance. The test starts at a stress of 0.1 kPa for 10 creep/recovery cycles, and then the stress is increased to 3.2 kPa and repeated for an additional 10 cycles. The typical results of this test as shown in Fig. 6, can be used to calculate the percent recovery and non-recoverable creep compliance. The non-recoverable creep compliance at multiple stress levels is an indicator of the sensitivity to permanent deformation and stress dependence of bituminous binders.

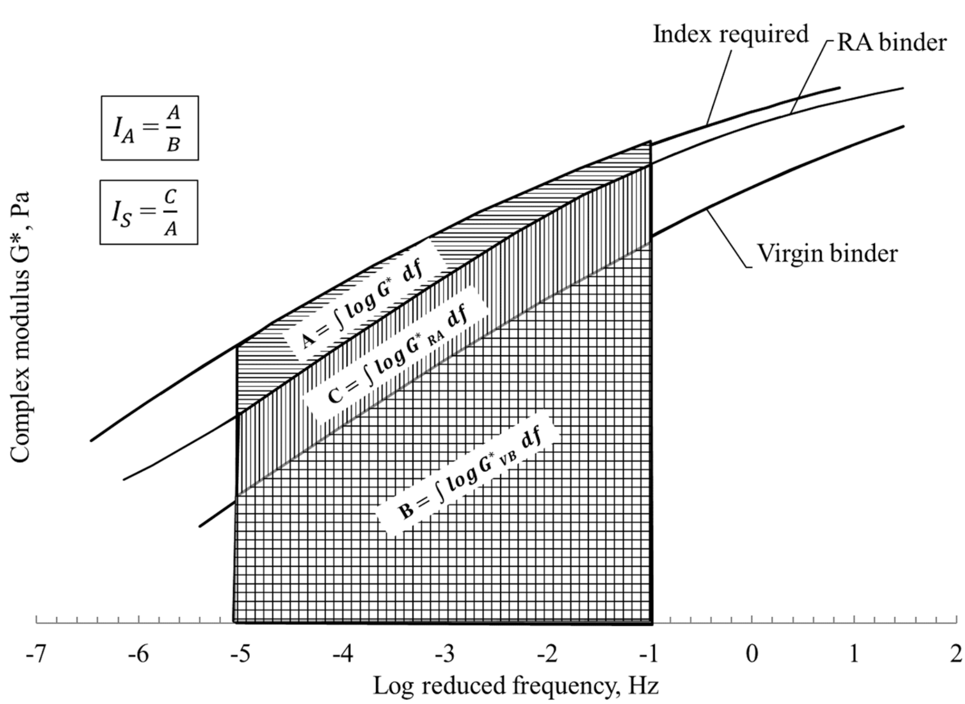


Fig. 5. Principle of indices calculation from complex modulus mastercurves.

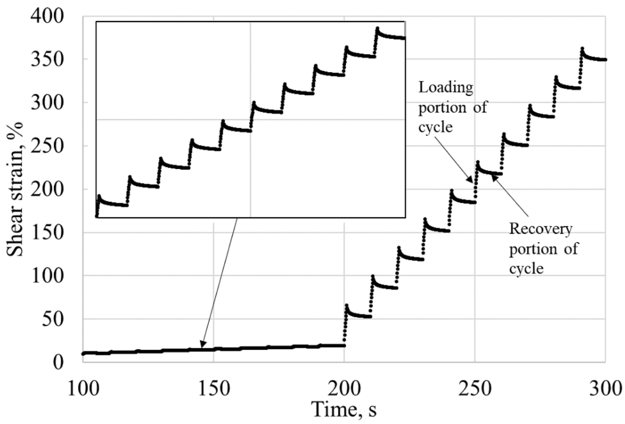


Fig. 6. Typical results from multiple stress creep recovery test.

3.3.4. Fourier transform infrared spectroscopy analysis

The reaction of asphalt with oxygen is accompanied by the production of functional groups including ketones, anhydrides, carboxylic acids, and sulfoxides [48]. These chemical functionalities can be identified based on absorption intensities using FTIR spectroscopy [49,50]. Attenuated total reflectance (ATR) based FTIR spectroscopy analysis was used to evaluate the changes in functional groups of the binder at different aging stages. In this test, the spectra for all the bitumen samples were recorded using VERTEX 70v Spectrometer with diamond crystal. A background scan of crystal was performed on empty crystal before each measurement. To conduct the test, a small quantity of recovered bitumen sample at room temperature was placed on the crystal using a metal spatula. The spectra were collected between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1} with 16 scans for each measurement. For each type of binder, four samples were tested. The binder spectra were subjected to max–min normalisation around the main band observed in wavelength of 2800 to 3200 cm^{-1}. From the normalised spectra, the carbonyl index ($I_{C=O}$) and sulfonyl index ($I_{S=O}$) were calculated using

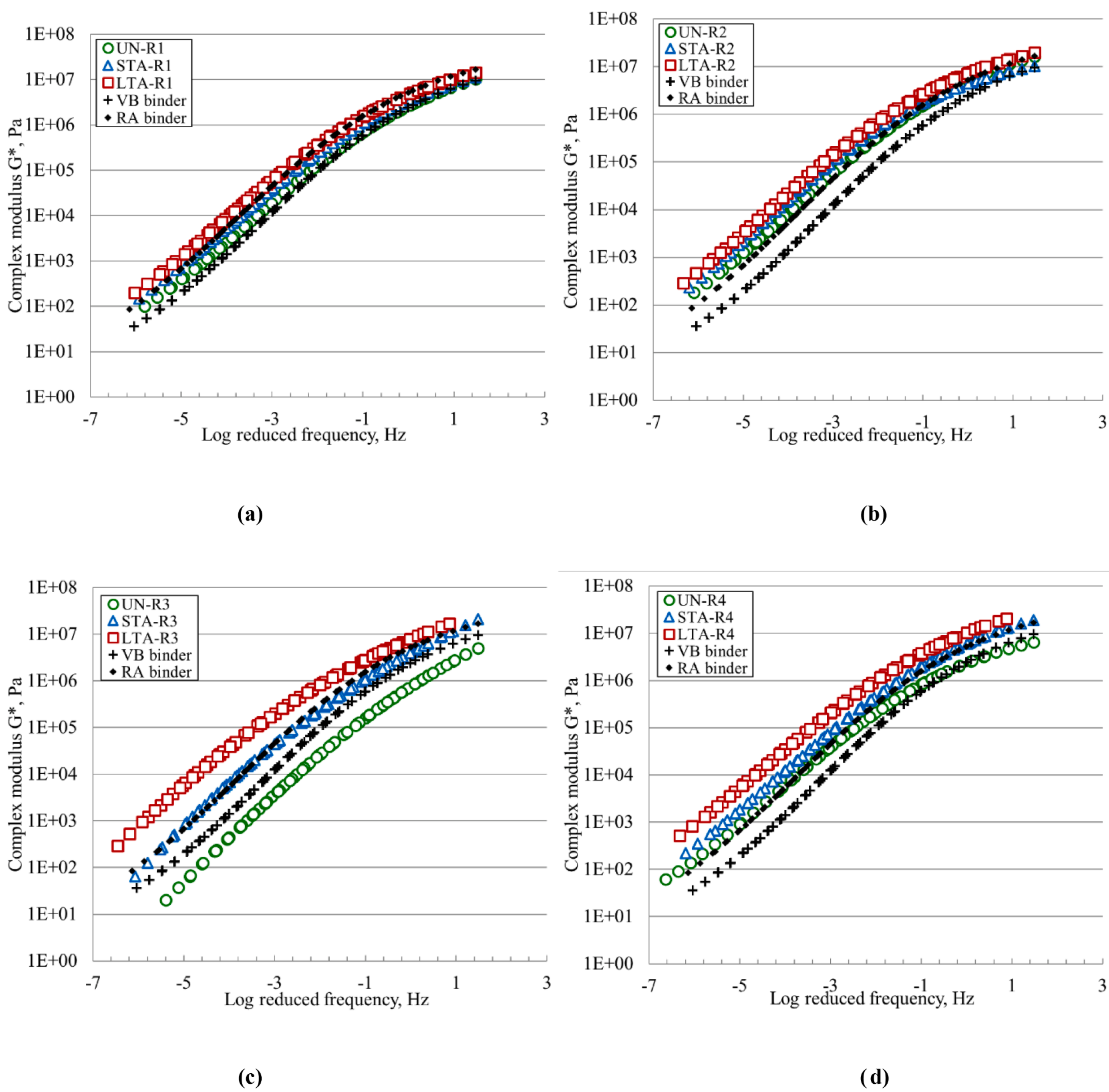


Fig. 7. Complex modulus mastercurves at 20 °C for rejuvenator (a) R1; (b) R2; (c) R3; (d) R4.

baseline integration. Both these indices are a ratio of areas where the numerator part was the value obtained from baseline integration of normalised spectra in the region 1660 cm^{-1} to 1720 cm^{-1} and 1100 cm^{-1} to 920 cm^{-1} for carbonyl index ($I_{C=O}$) and sulfonyl index ($I_{S=O}$) respectively. The denominator part for both the indices was the baseline integration of reference group which was in the range 1470 cm^{-1} to 1400 cm^{-1}.

4. Results and discussion

4.1. Complex modulus mastercurves

Fig. 7 shows the complex modulus (G*) mastercurves at reference temperature of 20 °C for all the bitumen samples in this study. The effect of aging the mixtures can be seen from increase in complex shear modulus over wide range of frequencies. An increase in complex modulus indicates the stiffening of bitumen, which occurs due to increase in the asphaltenes/maltenes ratio in bitumen with aging. It is also seen from Fig. 7, that in log scale, the increase in complex modulus with aging is more prominent at low frequencies (or high temperatures) as compared to high frequencies (or low temperatures) for all the bitumen, except for the R4. This may indicate that in long-term, most of rejuvenators (tall oil based, vegetal oil and polymer-based, and bio oil-based) benefit more the low-temperature performance by causing less change in stiffness of bitumen at low temperatures compared to high temperatures. The rejuvenator used in R4 was petroleum based and was less effective in improving the long-term low-temperature performance compared to other rejuvenators used in this study.

The aging of bitumen shows significant impact on the rheological properties of asphalt [36,51,52]. To quantify the effect of rejuvenators on aging, an aging index (I_A) was developed in this study based on area calculation over a wide range of frequencies. This index gives an indication about degree of aging in binder with reference to degree of aging in virgin bitumen. The numerical value $I_A > 1$ indicates that stiffness of a bitumen sample over a selected range of frequencies is higher than the stiffness of virgin binder. Similarly, $I_A < 1$ indicates that stiffness of a bitumen sample is lower than the stiffness of virgin binder. Therefore, the aging index for virgin binder will be unity in this case. It can be seen from Fig. 8, that in unaged condition, except R3 all the bitumen show values $I_A > 1$. This means that except R3, none of rejuvenators reduced stiffness of bitumen in unaged condition such that the resultant stiffness was lower than virgin bitumen stiffness. However, for R3, a dramatically high reduction in stiffness of bitumen ($I_A = 0.27$) was observed. This indicates that bio oil-based rejuvenator (R3) may provide high softening of binder and stiffness reduction in unaged condition. I_A for R1 was closest to unity, which indicates that this rejuvenator reduced stiffness of binder to a level reaching stiffness nearest to the virgin binder. The least reduction in stiffness of bitumen in unaged condition (indicated by highest $I_A = 3.05$), among all the four rejuvenators was observed for R2 suggesting the lowest softening achieved in this case with vegetal oil and polymer-based rejuvenator.

After short-term aging (see Fig. 8), the difference in aging index among all the four bitumen was reduced. The highest degree of aging was present in R2 ($I_A = 4.02$) followed by R4 ($I_A = 3.92$), which is similar to the aging index ranks of these binders in unaged state. However, the I_A values for these bitumen samples were very close, indicating less difference in stiffness of bitumen. Similarly, I_A for R3 was almost equal to that of R1. This indicates that stiffness of binder achieved after short-term aging was equivalent for R1 and R3, as well as for R2 and R4.

All the long-term aged binders showed a very high difference in I_A values among each other, which suggests that rejuvenators play an important role in governing the long-term stiffness of the bitumen. The tall oil-based rejuvenator (R1) showed lowest I_A value among all binders indicating least stiffness of this binder achieved after long-term aging, which could be a positive sign for long term low-temperature performance of this binder. On other hand, petroleum-based rejuvenator (R4) showed highest I_A value indicating highest stiffness of binder achieved in this case after long-term aging. It should be noted that the highest different between aging index of unaged and long-term aged binder was observed for R4 (6.51), while lowest difference was observed for R1 (1.86). This shows that in long-term, the tall oil-based rejuvenator (R1) was most effective and petroleum-based rejuvenator (R4) was least effective in reducing the stiffness of bitumen.

Another indicator known as softening index (I_S) was calculated in this study, which is very similar to aging index, except the comparison is made with RA binder as a reference. Therefore, the I_S values will indicate the change in stiffness of bitumen with respect of RA binder. $I_S > 1$ indicates stiffness of a bitumen sample over a selected range of frequencies is lower than the stiffness of RA binder. Similarly, $I_S < 1$ indicates that stiffness of a bitumen sample is higher than the stiffness of RA binder. Therefore, the softening index for RA binder will be unity in this case. It can be seen from Fig. 9, that except R2, all the rejuvenators in unaged stage reduced the stiffness of bitumen to a level ($I_S > 1$) that was lower than the stiffness of RA binder. For R2, the unaged binder stiffness was almost equivalent ($I_S = 0.95$) to that of RA binder stiffness. This shows that vegetal oil and polymer-based rejuvenator (R2) did not provide any significant reduction in stiffness of the binder. After, short-term aging except R1 ($I_S = 1.41$), all the bitumen aged to a level above the RA binder ($I_S < 1$), which indicates that stiffness reduction was lost after short-term aging except in the binder with tall oil-based rejuvenator (R1). Further after long-term aging, the aging level in R1 was also reached above the aging level of RA binder, but the highest I_S value for R1 ($I_S = 0.94$) indicates that retained effect of stiffness reduction was highest for this mixture containing tall oil-based rejuvenator compared to others in the long-term.

Overall, in long-term none of the rejuvenators used in this study could retain the reduced stiffness of bitumen obtained from rejuvenator addition to level below the RA binder stiffness. Additionally, the

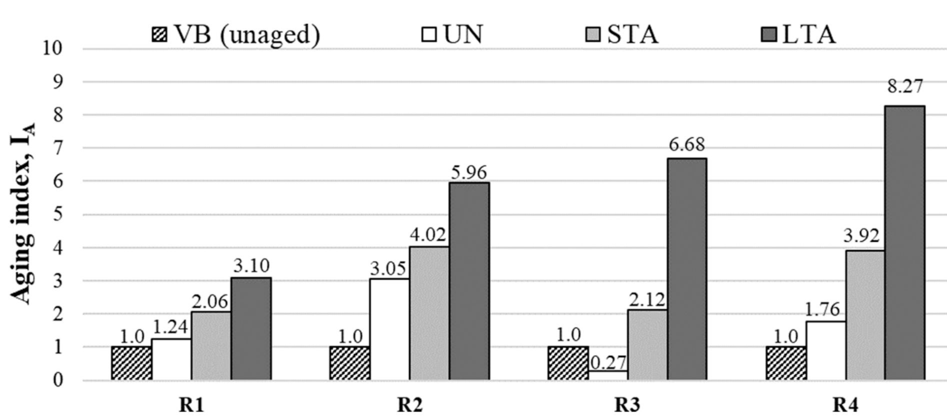


Fig. 8. Aging index for bitumen samples at different aging stages.

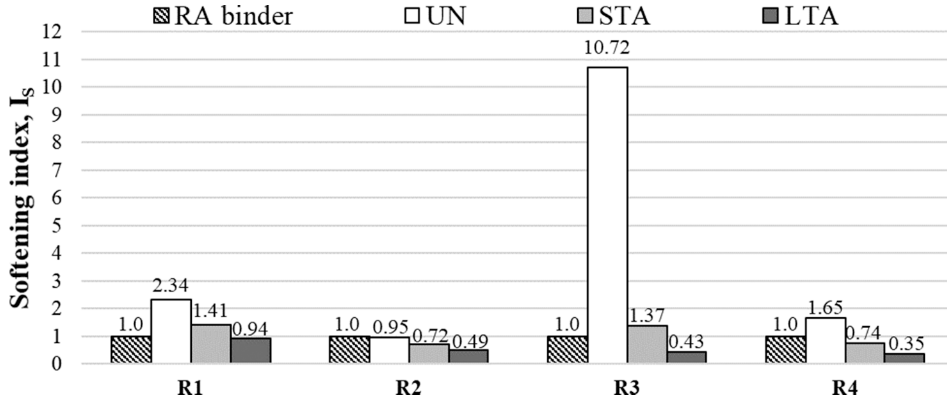


Fig. 9. Softening index for bitumen samples at different aging stages.

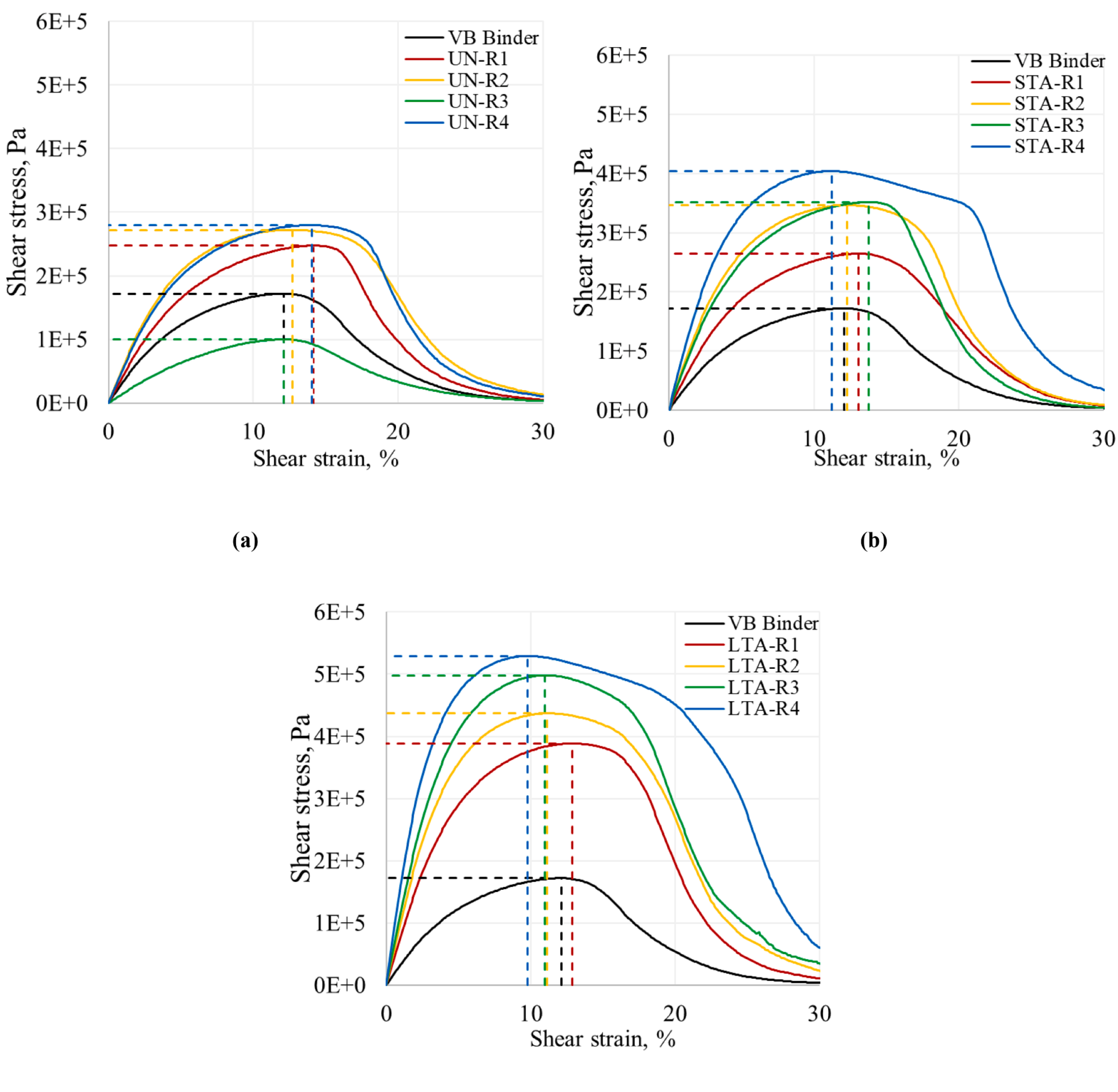


Fig. 10. Shear stress vs strain curve for 100% RA binders and virgin bitumen.

variation in aging and softening indices for all the bitumen samples at different aging stages shows that level of aging can vary significantly for different rejuvenators. Therefore, performance of mixtures produced using these rejuvenators can be extremely sensitive to mixture aging.

4.2. Fatigue resistance

Fig. 10 shows the plots of shear stresses versus strain from linear amplitude sweep (LAS) test at a temperature of 25 °C. It can be seen from Fig. 10a-c that the peak stress for all the unaged bitumen samples increased with short-term aging, and further after the long-term aging, as a result of stiffening of binder. Compared to virgin bitumen (VB) as shown in Fig. 10a, all the unaged binders except R3, show a higher peak stress due to presence of RA binder. For UN-R3, the peak stress was low due to a high amount of softening from this rejuvenator as also observed from complex modulus mastercurves earlier. Further as seen in Fig. 10a, the strains corresponding to peak stresses in all the unaged bitumen samples were equal or higher compared to strain in virgin binder. However, after long-term aging (see Fig. 10c), the strains in all the samples except R1, turn out to be lower compared to the strain in virgin binder. This implies the fact that the softer binders (unaged) exhibit lower peak stress, but higher deformation compared to the stiff binders (aged). As seen in Fig. 10c, both peak stress and corresponding strain were higher in LTA-R1 compared to VB, which could be a positive effect of R1 rejuvenator modification, as this binder may be able to undergo a greater number of cycles to fatigue failure at higher strains. However, the strain tolerance of binder indicates the fatigue performance only to a certain extent. Therefore, fatigue damage analysis was conducted for more information about the fatigue properties of binders.

Fig. 11 shows the plot of predicted number of cycles to fatigue failure (N_f) for all the binders calculated using VECD model for a range of strain levels. The number of cycles for fatigue failure for 2.5% and 5% strain

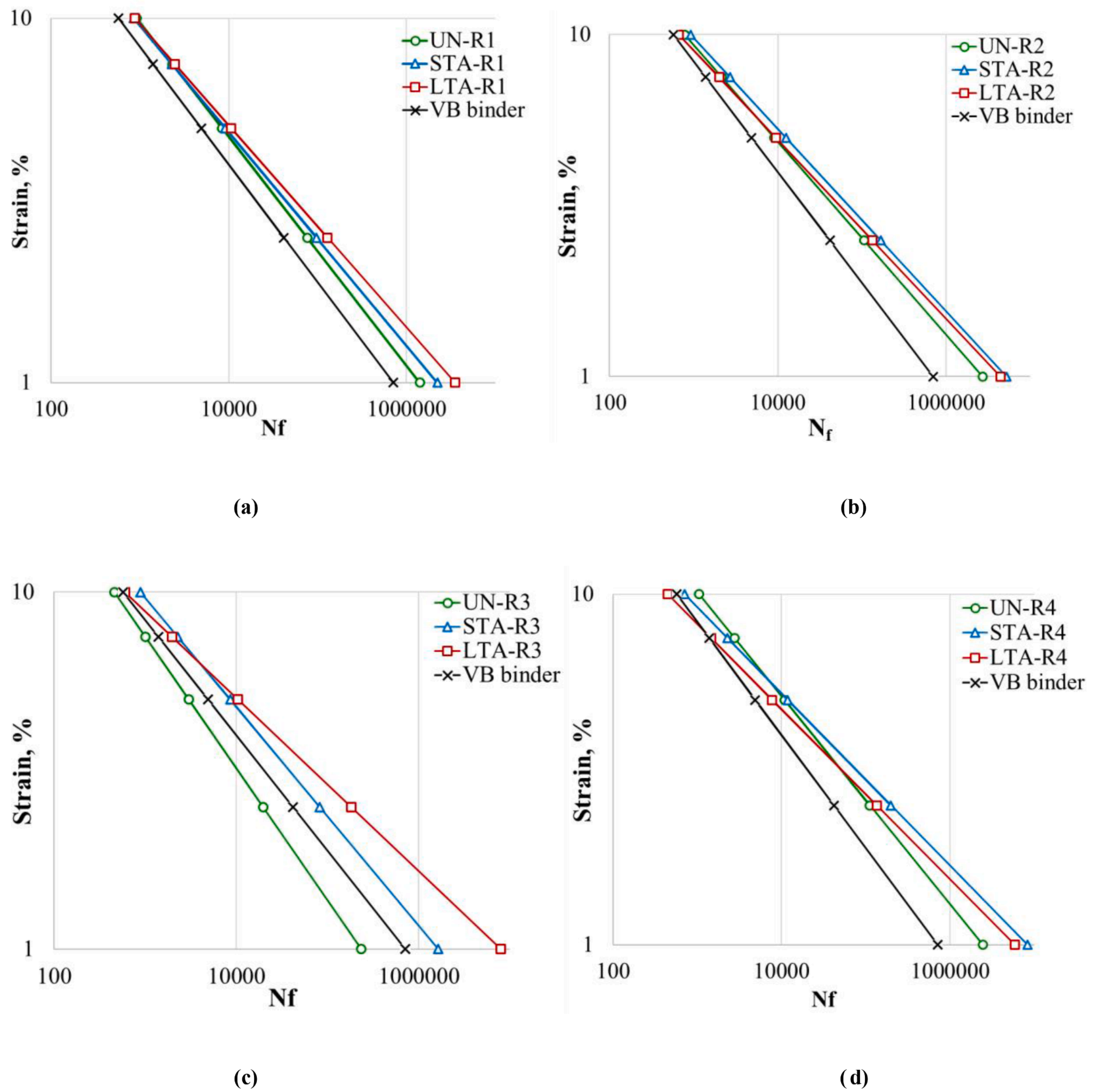


Fig. 11. Fatigue life vs strain relationship.

levels is shown in Table 3. The fatigue lives for all the unaged bitumen samples (except UN-R3) were higher than the virgin binder, at both the strain levels. This was due to higher stiffness achieved in unaged bitumen samples compared to virgin bitumen that benefitted their fatigue life. The softening achieved in binder modified using rejuvenator R3 was higher compared to virgin binder, as a result, fatigue life of UN-R3 turned out to be lower at various strain levels.

After short-term aging, all four bitumen samples showed higher fatigue lives compared to unaged state, at both 2.5% and 5% the strain levels (see Table 3). The short-term aging significantly increased the stiffness of the binder facilitating the bitumen to undergo higher number of cycles until fatigue failure. The lowest increment in fatigue life after short-term aging was observed for R1 (27% and 8% at 2.5% and 5% strain level, respectively). However, this is not a disadvantage for R1 as it already shows much higher fatigue life than the virgin binder.

After long-term aging, the fatigue life for R2 and R4 were reduced, while fatigue life for R1 and R3 were increased as compared to short-term aged samples. Though, the stiffnesses of both R2 and R4 bitumen were increased after the long-term aging as seen in Fig. 7 earlier, there may be a loss in elastic compounds in these bitumen samples that resulted in higher damage and reduction in number of cycles to fatigue failure. This could indicate that tall oil based (R1) and bio oil-based (R3) rejuvenators are more beneficial for long-term fatigue performance of bitumen compared to vegetal oil and polymer based (R2) and petroleum-based (R4) rejuvenators. In long term, R1 showed the lowest fatigue life at 2.5% strain level but highest fatigue life at 5% strain, which indicates that when used in thin pavements, tall oil based (R1) rejuvenator can provide better fatigue resistance compared to other rejuvenators. Similarly for thick pavements, the bio oil-based rejuvenator (R3) may be providing highest fatigue life in the long-term as the fatigue life for this binder was highest at 2.5% strain level.

As observed in this study, long-term aged bitumen at lower strain level (2.5%) showed higher fatigue life than unaged bitumen, which may not be completely accurate in field conditions. This outcome could be affected due to limitation of the test adopted, as fatigue damage does not occur solely due to cohesive damage, but also due to loss of adhesion between bitumen and aggregates [27]. The oxidation of bitumen may improve fatigue life due to increased stiffness but also reduces it by weaking the bond between bitumen and aggregates. In this case the high stiffness is the fundamental parameter associated with fatigue life instead of elastic recovery properties [53]. Therefore, further investigations are required to understand the effect of aging on fatigue behaviour of binder and mixtures with 100% reclaimed asphalt.

4.3. Rutting resistance

Multiple stress creep recovery test (MSCRT) was conducted at 0.1 kPa and 3.2 kPa stress levels. These stress levels do not necessarily represent the nonlinear stress levels in binder, but a higher stress level may predict the rutting resistance more clearly [54]. Therefore, the results of non-recoverable creep compliance and percent recovery from multiple stress creep recovery test at 3.2 kPa stress level have been reported. Lower values of non-recoverable creep compliance (J_{nr}) in bitumen have been correlated to better rutting performance of the mixtures [55]. The percent recovery is a measure of recoverable viscoelastic strain in creep portion after removal of shear stress. As shown in Fig. 12, in unaged (UN) conditions, R1 and R3 showed considerably higher J_{nr} values compared to other bitumen. Additionally, R1 and R3 did not show any percent recovery in unaged conditions as shown in Fig. 13. Therefore, the bitumen samples modified using tall oil based (R1) and bio-oil based (R3) rejuvenator may be more susceptible to rutting compared to other binders in unaged condition. However, this does not mean that R1 and R3 binders will show poor rutting performance. In fact, the J_{nr} for R1 and R3 was almost equal to that of J_{nr} of virgin bitumen, which also did not show any percent recovery, which indicates these bitumen samples in unaged condition may show same rutting performance as that of virgin binder.

The short-term aging (STA) of mixtures has considerably reduced the J_{nr} value and increased the percent recovery for all the bitumen, which indicates that the oxidation of bitumen during short-term aging can considerably improve the high-temperature deformation resistance. After long-term aging, a further reduction in J_{nr} values and increase in percent recovery shows that these binders have undergone excessive stiffening that led to increased rutting resistance of bitumen. The long-term aged binders show different J_{nr} values indicating that even after aging, the binder containing different rejuvenators will have distinct rutting performance. Overall, all the bitumen samples show J_{nr} values within the permissible limits (4 kPa^{-1}) given by AASHTO MP 19–10 [56]. This confirms that rejuvenators do not inhibit the binder to fulfil the acceptable rutting performance in 100% RA mixtures.

Table 3
Predicted fatigue life from VEDC model for 2.5% and 5% strain levels.

Binder	UN		STA		LTA	
	2.5% N_f	5% N_f	2.5% N_f	5% N_f	2.5% N_f	5% N_f
VB Binder	41,812	4898	×	×	×	×
R1	76,546	8414	97,508	9125	129,223	10,652
R2	106,019	9073	168,539	12,494	135,006	9502
R3	19,535	2993	82,058	8523	181,708	10,433
R4	112,143	10,835	199,611	11,875	134,771	7767

4.4. Chemical characterisation

In this study, absolute baseline integration was performed on normalised spectra to calculate the carbonyl and sulfonyl indices, as best repeatability of FTIR results has been shown using this method [57]. An increase in carbonyl index has shown positive correlation with oxidation of bitumen in past studies [48–50]. It can be seen from Table 4 that carbonyl index values for all the unaged rejuvenated binders were higher than the carbonyl index of virgin binder (0.1). The higher index for these samples indicates higher binder aging level in these samples due to presence of reclaimed asphalt binder. The carbonyl peaks for rejuvenated samples can also be seen in region 1660 cm^{-1} to 1720 cm^{-1} in Fig. 14, while these peaks were not present in virgin binder. The peaks shown by three out of four rejuvenators around 1740 cm^{-1} wavelength in Fig. 4 earlier were also seen for rejuvenated binders R1 and R3 in all the three aging stages as shown in Fig. 14. For R2, this peak was observed only in unaged condition (UN-R2), and the diminishing peak for aged samples could be due to oxidation of rejuvenator. However, the peaks around this region could also be affected by oxidation of bitumen. After short-term aging, the binder is more oxidised and is expected to show an increase in carbonyl index. Surprisingly, after short-term aging, the carbonyl index for all the bitumen samples decreased. The difference may be either be due to material variability or it is possible that short-term aging of binder was not enough to show a considerable increase in carbonyl peak intensity. A study also found that the binder short-term aging simulation did not show any visible increase in carbonyl index, and a distinct band of carbonyl structures was detected only after long-term aging simulation of binder [58]. All the short-term aged bitumen samples showed equal carbonyl index with exception of STA-R4. This sample also showed unusually large sulfoxide peak in region 1100 cm^{-1} to 920 cm^{-1} which could be due to presence of filler residue in the recovered bitumen. As a result, the index calculation for this sample was confounded due to change in intensity of aliphatic band (reference group). After the long-term aging, the carbonyl indices of all the bitumen samples were increased as compared to short-term aged samples. This indicates that after long-term aging, a considerable increase in carbonyl peak intensity occurs. However, when comparing with unaged bitumen samples, R1, R3 and R4 showed slightly higher but R2 showed equal carbonyl index in long term aged bitumen. These inconsistencies may indicate that carbonyl peaks could also be affected due to presence

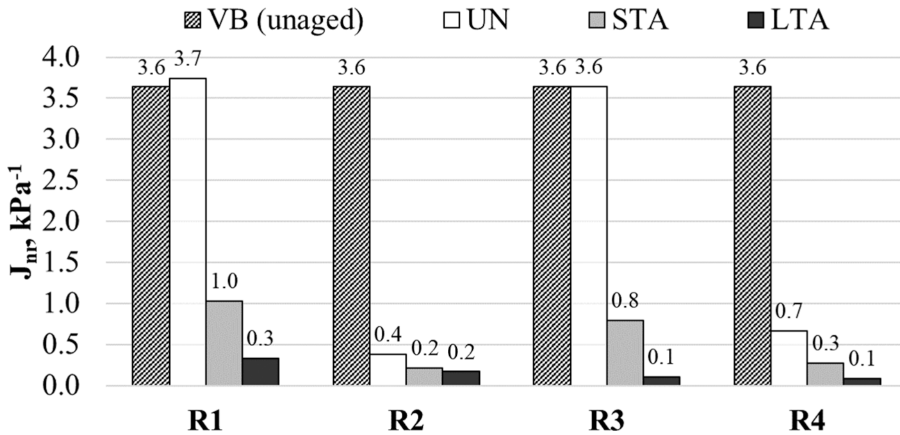


Fig. 12. Non-recoverable creep compliance (J_{nr}) from multiple stress creep recovery test at 60 °C.

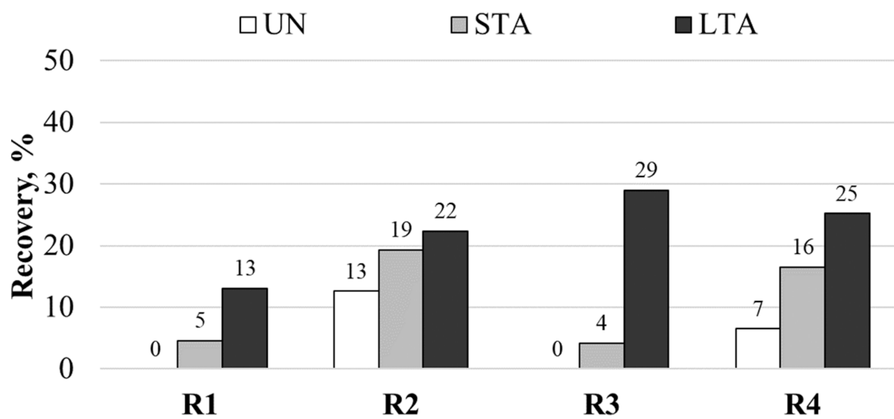


Fig. 13. Percent recovery from multiple stress creep recovery test at 60 °C.

Table 4
Calculation results of carbonyl indices from normalised spectrum.

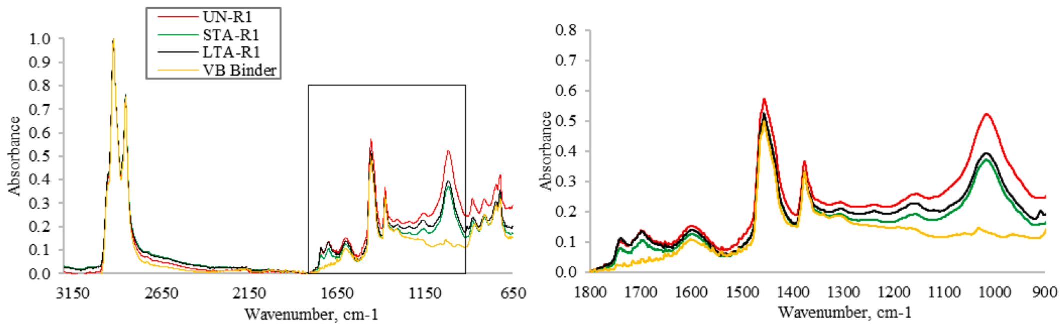
Material	Aging state	Average carbonyl index ($I_{C=O}$)	SD	Average sulphonyl index ($I_{S=O}$)	SD
VB	UN	0.10	0.005	1.20	0.108
R1	UN	0.20	0.009	1.93	0.364
	STA	0.17	0.018	1.56	0.045
	LTA	0.22	0.004	1.69	0.010
R2	UN	0.18	0.017	1.71	0.164
	STA	0.17	0.003	1.40	0.020
	LTA	0.18	0.004	1.57	0.031
R3	UN	0.18	0.007	1.57	0.075
	STA	0.17	0.004	1.69	0.063
	LTA	0.23	0.063	1.64	0.301
R4	UN	0.16	0.003	1.47	0.025
	STA	0.11	0.005	2.46	0.035
	LTA	0.18	0.017	1.65	0.049

of rejuvenator in the binder. For this reason, the assessment of carbonyl index in blends with rejuvenators is considered problematic [59]. Further as shown in Table 4, no clear trend can be observed for sulfoxide index of bitumen samples at different aging states. It was also observed in some of the previous research that the sulfoxide index is not an appropriate indicator of aging in the bitumen [60,61]. Overall, the known FTIR indices that reflect the aging state of bitumen need more investigation when characterising for reclaimed asphalt binder containing rejuvenators.

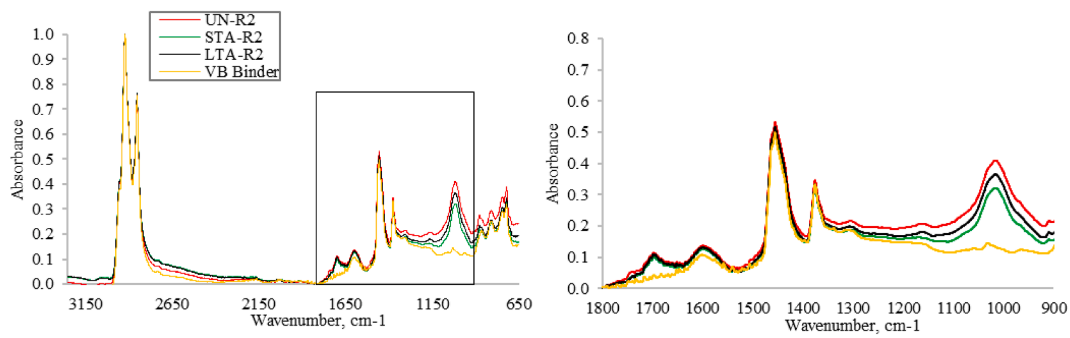
5. Conclusion

Using rheological and chemical analysis, the effect of rejuvenators on aging of 100% reclaimed asphalt mixtures was investigated. The aging was simulated on the mixtures which was followed by extraction of binder for analysis. The tests conducted in this study include temperature and frequency sweep, linear amplitude sweep, multiple stress creep recovery, and Fourier transform infrared spectroscopy. Based on the test results, the following conclusions are made:

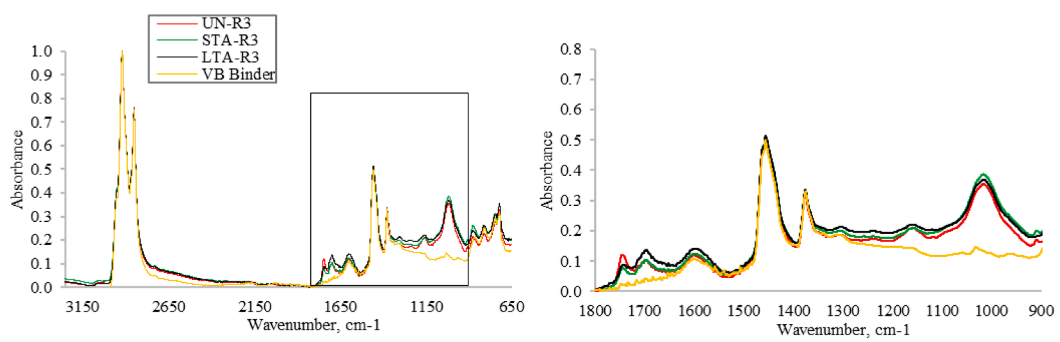
- From temperature-frequency sweep test, the effect of aging was seen as shift in complex modulus mastercurves for all the bitumen. The results showed that rejuvenators play important role in governing the long-term properties of rejuvenated bitumen. In long-term, the highest reduction in stiffness of bitumen was achieved by tall oil-based rejuvenator, while lowest reduction in stiffness was achieved by petroleum-based rejuvenator.
- From linear amplitude sweep test, the long-term aged bitumen showed much higher fatigue life than the unaged sample due to the increase in stiffness of the bitumen with aging. Considering the general view that fatigue damage may increase after long-term aging due to weakening of the bond between aggregates and the bitumen, the contradictory observation in this study indicates towards limitation of LAS test for fatigue performance evaluation of aged bitumen.
- The bitumen containing rejuvenators showed acceptable rutting performance and with aging the rutting performance of binders was enhanced due to stiffening of bitumen. The tall oil-based rejuvenator and bio oil-based rejuvenator showed higher rutting susceptibility of



(a)



(b)



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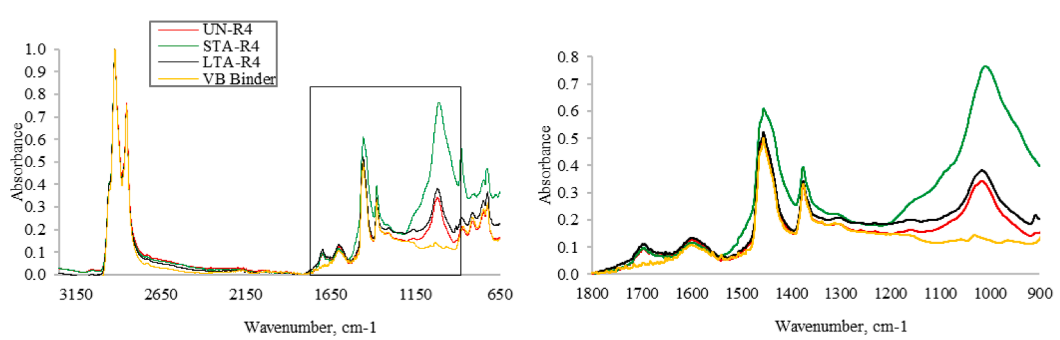

(d)

Fig. 14. FTIR spectra for all the rejuvenated binders used in this study along with magnified area in 900–1800 cm^{-1}.

binder compared to other rejuvenators, however these binders showed comparable rutting performance to virgin binder. The long-term rutting susceptibility of the binders was found to be affected by type of rejuvenator used in the mixture.

- The FTIR spectra for all the rejuvenated binders except the one containing petroleum-based rejuvenator, showed unique peaks in the same range where the peaks were observed for respective rejuvenators. The short-term aging of mixtures did not show a considerable increase in carbonyl peak intensity. However, after long-term aging an increase in carbonyl index was observed for all the four binders.

To sum up, this study showed that different rejuvenators age in a distinct way, which implies the importance of considering the long-term performance of bitumen for selection of a rejuvenator. Dynamic shear rheometer can be used to quantify the degree of aging from change in stiffness of bitumen. However, the conventional binder performance tests using dynamic shear rheometer have some limitations and may not truly represent the aging characteristics of stiff materials like high reclaimed asphalt content mixtures. Therefore, further studies should develop new methods for binder performance evaluation that show good correlation with field performance of high reclaimed asphalt content mixtures. It is also important to compare the progressive aging in conventional mixtures with reclaimed asphalt mixtures containing rejuvenator to calculate the benefits of using rejuvenators during the entire life cycle of the pavement. The future studies may also explore the long-term effect of rejuvenators on low-temperature performance of reclaimed asphalt mixtures.

CRediT authorship contribution statement

Mukul Rathore: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Viktors Haritonovs:** Supervision, Resources, Writing – review & editing. **Remo Merijs Meri:** Supervision, Resources, Writing – review & editing. **Martins Zaumanis:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

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

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