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Evaluating the ageing degrees of bitumen by rheological and chemical indices

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ABSTRACT

The ageing of bitumen is an inevitable phenomenon which is still challenging to be characterised. This paper aims at evaluating the ageing degrees of bitumen comprehensively. There were six types of bitumen being aged to five levels for comparing purposes and multiple rheological tests by a DSR as well as chemical test for the SARA (saturates, aromatics, resins and asphaltenes) properties of bitumen were carried out. The critical temperatures, *G-R* parameter and nonrecoverable-compliance-based ageing indices were proposed to evaluate the ageing degrees of bitumen in terms of low-, intermediate- and high-temperature performance of bitumen, respectively. Also, a novel ageing evaluation index based on the integration of modulus of master curves was employed and modified, which can evaluate the ageing degrees of bitumen accurately in terms of the whole range of temperature. Finally, the chemical ageing index were analysed and was confirmed to have strong linear relationship with rheological indices of bitumen.

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KEYWORDS
Bitumen; ageing; rheological properties; chemical properties; ageing index

1. Introduction

Bitumen is one of the most crucial construction materials used in the infrastructure. However, owing to the complex physical and chemical reactions with oxygen and other oxynitride, bitumen undergoes intricate chemical component migration and microstructure transformation, leading to the ageing of binders and thereby further performance deteriorates (Petersen et al., 1994), severely affecting its usability and overall performance (Alae et al., 2021; Hofko et al., 2015; Omairey et al., 2022).

Bitumen ageing mainly occurs during (1) the mixing, transport and paving activities, which is known as short-term ageing and can be simulated by rolling thin film oven test (RTFOT), and (2) the entire service life which is known as long-term ageing, involving the exposure to traffic and exhaust gas but also the impact of environmental aspects like temperature, weather and radiation and can be simulated by pressure ageing vessel (PAV) (Jing et al., 2021; Mirwald et al., 2020). It is well recognised that the irreversible changes triggered by oxidative and thermal ageing accumulating over time are impairing the durability and usability of asphalt pavement as the aged binders are more susceptible to cracking even pothole (Siroma et al., 2022). On top of the challenge to distinguishingly age the bitumen to differentiate the deterioration of performance in terms of ageing degrees, the efficient and comprehensive indices are required to characterise the actual performance of binders affected by ageing (Hu et al., 2022). Since bitumen is a temperature-sensitive material, the performance characterisation is thereby

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Table 1. Fundamental information of the materials.

Binders	Penetration (0.1 mm)	Softening point (°C)	PG	Continuous PG	Viscosity (135°C) (mPa s)
Neat 40/60A	41	52.7	PG 70-16	PG 75.6-21.1	366.5
Neat 40/60B	45	51.5	PG 70-16	PG 71.5-21.3	374.9
Neat 40/60C	57	50.0	PG 70-22	PG 73.3-22.2	376.7
Neat 70/100D	81	45.4	PG 64-22	PG 67.8-27.4	305.9
Neat 70/100E	83	46.0	PG 70-22	PG 71.8-25.2	292.7
Neat 70/100F	86	44.4	PG 64-22	PG 64.0-25.8	263.3

conducted at different temperatures by different evaluation indices (Hossain et al., 2016; Wang et al., 2019, 2021). In terms of the chemical properties of bitumen, a shift within the SARA (saturates, aromatics, resins and asphaltenes) fractions can be observed with an increasing amount of asphaltenes and decreasing amount of aromatics over time (Hofko et al., 2016), this is the interior reason why bitumen is stiffer and stiffer with the ageing ongoing.

The question of how the chemical components and the mechanical properties are linked has been of interest to academics for decades (Eberhardsteiner et al., 2015). However, it is still challenging to disclose the real performance evolution of bitumen in terms of ageing. Some indices were put forward and either has been applied in some cases or declaimed to have poor correlations with actual situations. Therefore, the investigation on novel, performance-based and universally applicable indices is always ongoing. The ubiquitous problem for most conventional indices is they usually use one point (moduli, phase angles or stiffness, etc. at a dedicated temperature and frequency) to illustrate the performance of binders, which makes it inevitably arbitrary sometimes due to various errors. Also, only one point is not eligible to demonstrate the highly temperature-sensibility of bitumen. Motivated by this, this research aims at evaluating the ageing degrees of bitumen by some more comprehensive factors, for example, the range of complex moduli rather than just one complex modulus to have a further recognition of the ageing behaviour of bituminous binders in terms of their high-, intermediate- and low-temperature performance. Finally, the chemical properties of bitumen will be utilised to verify the reliability of the proposed rheological ageing indices therefore to give a better understanding of the ageing of bitumen.

2. Materials and methods

2.1. Materials

The materials used in this study were three penetration grade 40/60 bitumens and three penetration grade 70/100 bitumens; the fundamental properties of the bitumens are listed in Table 1.

2.2. Ageing procedures

The standard RTFOT test at 163°C for 85 min was applied (BSI, 2014). Then, the residuum was subjected to the PAV (BSI, 2012a). In addition to the standard PAV for 20 h at 2.1 MPa and 100°C, this study also employed 15, 30 and 40 h as the ageing lasting periods.

2.3. Chemical properties tests

The chemical components of bitumen were detected by thin-layer chromatography with flame ionisation detection (TLC-FID). The principle of this test is separating the generic fractions of bitumen in terms of their solubility in dedicated solvents. For example, the saturates were separated from other more polar components due to its good solubility in *n*-heptane and weak strength of interaction with the adsorbent (silica); it is the same for aromatics and resins. Finally, the most polar and insoluble asphaltenes were left at the bottom of the chromarods.

First, the bitumen was dissolved in dichloromethane to get a solution with a concentration of 2% (weight/volume). Then, 1 µl of the solution was spotted carefully on the zero scale of the chromarods by a dedicated micro dispenser. Prior to this, the chromarods were cleaned by running through FID flame twice to remove any residue left previously. Then, the SARA fractions separation was carried out in three phases in development tanks which consists of *n*-heptane; 80/20 toluene/*n*-heptane blend and 95/5 blend of methylenedichloride/methanol for the saturates, aromatics and resins, respectively. The chromarods were developed in succession in each of the solvents. Then the chromarods were dried in the oven for 90 s at 80°C. The dried chromarods were scanned in the machine at a frequency of 40 scans/s. The air and hydrogen flow rates were set at 2 l/min and 160 ml/min, respectively. The scanned output of the FID is plotted vs the chromarod peaks which are attributed to SARA fractions from which the weight proportions of each fraction are determined (Lu et al., 2008).

2.4. Rheological properties evaluation

Bending beam rheometer test. The bending beam rheometer (BBR) tests were conducted from 0°C to −24°C, interval 6°C, depending on the estimated stiffness and *m*-value of specimens, as per BS EN 14771 (BSI, 2012c).

Multiple stress creep and recovery test. The multiple stress creep and recovery (MSCR) test was conducted on a dynamic shear rheometer at 64°C with a configuration of 25 mm parallel plates and 1 mm gap as per BS EN 16659 (BSI, 2015). The specimen was loaded at a constant creep stress of 0.1 kPa for 1 s duration creep and followed by a zero-stress recovery period of 9 s duration. The procedure was repeated for 10 cycles without any rest period. Subsequently, another 10 cycles were repeated at a load of 3.2 kPa without rest period.

Frequency sweep. The frequency sweep was conducted at a constant stain level of 0.1% for long-term aged binders, 0.4% for short-term aged binders and 0.5% for virgin binders, which was determined by an amplitude sweep to ensure the bitumen in a linear viscoelastic (LVE) response under the temperature ranges from 10 to 50°C, internal 10°C as per BS EN 14770 (BSI, 2012b). The geometry configuration was 8 mm plates with a gap of 2 mm.

3. Results and discussions

3.1. Low-temperature rheological performance

Previously, the stiffness (*S*), creep rate (*m*-value) as well as corresponding lower PG grades were used to characterise the low-temperature performance of binders. It is known that lower stiffness and higher creep rate indicate better resistance to thermal cracking. However, the lower PG is too rough to characterise the actual low-temperature performance of binders since the interval of different PGs up to 6°C. Therefore, a continuous index is needed to accurately characterise the performance of binders. Corresponding to the *S* and *m*-value, respectively, there are two critical temperatures for each binder. One is controlled by *S* ($T_{C,S}$) and another is controlled by *m* ($T_{C,m}$). The difference between $T_{C,S}$ and $T_{C,m}$ was defined as ΔT_c, as per ASTM D7643 (ASTM, 2022). It is obvious that if the ΔT_c is positive, the stiffness dominates the cracking behaviour of binders, vice versa (Rebecca & Anderson, 2001). The critical temperature could be calculated by Equations (1) and (2) as shown in Table 2.

$$T_{C,S} = T_1 + \frac{(T_1 - T_2)(\log 300 - \log S_1)}{\log S_1 - \log S_2} - 10, \tag{1}$$

$$T_{C,m} = T_1 + \frac{(T_1 - T_2)(0.3 - m_1)}{m_1 - m_2} - 10, \tag{2}$$

where $T_{C,S}$ and $T_{C,m}$ are the critical temperature controlled by stiffness and *m*-value, S_1 and S_2 are the stiffness which pass or fail the criterion (less than 300 MPa), m_1 and m_2 are the *m*-values which pass or

Table 2. Critical temperatures of different binders in different ageing situations.

Binders	Polarity	$T_{C,S}$ (°C)	$T_{C,m}$ (°C)	ΔT_C (°C)	Binders	Polarity	$T_{C,S}$ (°C)	$T_{C,m}$ (°C)	ΔT_C (°C)
Neat 40/60A	Virgin	−25.71	−26.90	1.19	Neat 70/100D	Virgin	−32.32	−32.56	0.24
	RFTOT	−23.94	−21.69	−2.25		RFTOT	−30.54	−30.77	0.23
	PAV15	−23.77	−19.79	−3.98		PAV15	−28.59	−27.76	−0.83
	PAV20	−23.40	−18.70	−4.70		PAV20	−27.90	−26.97	−0.93
	PAV30	−22.56	−16.39	−6.17		PAV30	−26.73	−25.44	−1.29
	PAV40	−22.44	−13.07	−9.37		PAV40	−26.27	−24.89	−1.38
Neat 40/60B	Virgin	−26.22	−27.13	0.92	Neat 70/100E	Virgin	−27.76	−29.39	1.63
	RFTOT	−24.46	−24.53	0.07		RFTOT	−26.52	−26.69	0.17
	PAV15	−22.89	−20.66	−2.23		PAV15	−25.77	−25.42	−0.35
	PAV20	−22.66	−19.90	−2.76		PAV20	−25.57	−24.90	−0.67
	PAV30	−22.16	−19.21	−2.95		PAV30	−25.38	−24.62	−0.76
	PAV40	−22.00	−18.25	−3.75		PAV40	−25.06	−23.22	−1.84
Neat 40/60C	Virgin	−24.61	−25.89	1.28	Neat 70/100F	Virgin	−28.39	−29.62	1.23
	RFTOT	−23.76	−24.91	1.15		RFTOT	−27.16	−27.28	0.12
	PAV15	−22.63	−22.60	−0.03		PAV15	−26.25	−25.95	−0.30
	PAV20	−22.43	−22.09	−0.34		PAV20	−25.99	−25.57	−0.42
	PAV30	−22.14	−21.71	−0.43		PAV30	−25.73	−24.97	−0.76
	PAV40	−21.77	−20.02	−1.75		PAV40	−25.35	−22.68	−2.67

fail the criterion (more than 0.300), T_1 and T_2 are the temperatures at which the stiffness or *m*-value passes or fails the criteria.

It can be seen from Table 2 that with ageing ongoing, the critical temperatures alter to a higher value for all binders, which means that the low-temperature performance of bitumen gets worse due to ageing. However, the improvement of critical temperatures is not dramatical. Moreover, the ΔT_c for the same binder tends to be more significant owing to the hardening and embrittling of bitumen. It is noteworthy that for the virgin binders and short-term aged binders (except Neat 40/60A), the ΔT_c is positive, which means that the thermal cracking is stiffness controlled, the damage occurs owing to the hardening of binders and losing of flexibility. It is opposite for the long-term aged binders, and the embrittling of binders contributes to the cracking of materials. Therefore, ageing alters the mechanism of cracking behaviour of neat bitumen, which switches from 'hardening' damage to 'embrittling' damage. Moreover, the absolute value of ΔT_c is getting larger with the ongoing of long-term ageing, which means that longer ageing lasting period has a severer impact on the thermal cracking behaviour of bitumen (Wang et al., 2019).

Comparing the T_c of binders at different long-term ageing periods, it was found that the $T_{C,m}$ is more sensitive to ageing. To evaluate the ageing degrees of bitumen in terms of the low-temperature performance, the low-temperature ageing index (LAI) was proposed. As forementioned, the *m*-value dominates the critical temperature of aged bitumen, therefore, it is suggested to use the $T_{c,m}$ to calculate the LAI, as per Equation (3) and shown in Figure 1(a). For comparison reason, the LAI based on $T_{c,s}$ is also employed, as per Equation (4) and shown in Figure 1(b).

$$\mathrm{LAI}_m = \frac{T_{c,m,V} - T_{c,m,A}}{T_{c,m,V}} \times 100\%, \tag{3}$$

$$\mathrm{LAI}_S = \frac{T_{c,S,V} - T_{c,S,A}}{T_{c,S,V}} \times 100\%, \tag{4}$$

where $T_{c,m,A}$ and $T_{c,S,A}$ refer to the T_c controlled by *m*-value and stiffness, respectively, for aged binders and $T_{c,m,V}$ and $T_{c,S,V}$ refer these to virgin binders.

It was found in Figure 1(a,b) that ageing weakens the low-temperature performance of binders based on the critical temperatures. Both indices are eligible to characterise the ageing degree of bitumen. To verify the coordination and effectiveness of these two indices, the correlation between these

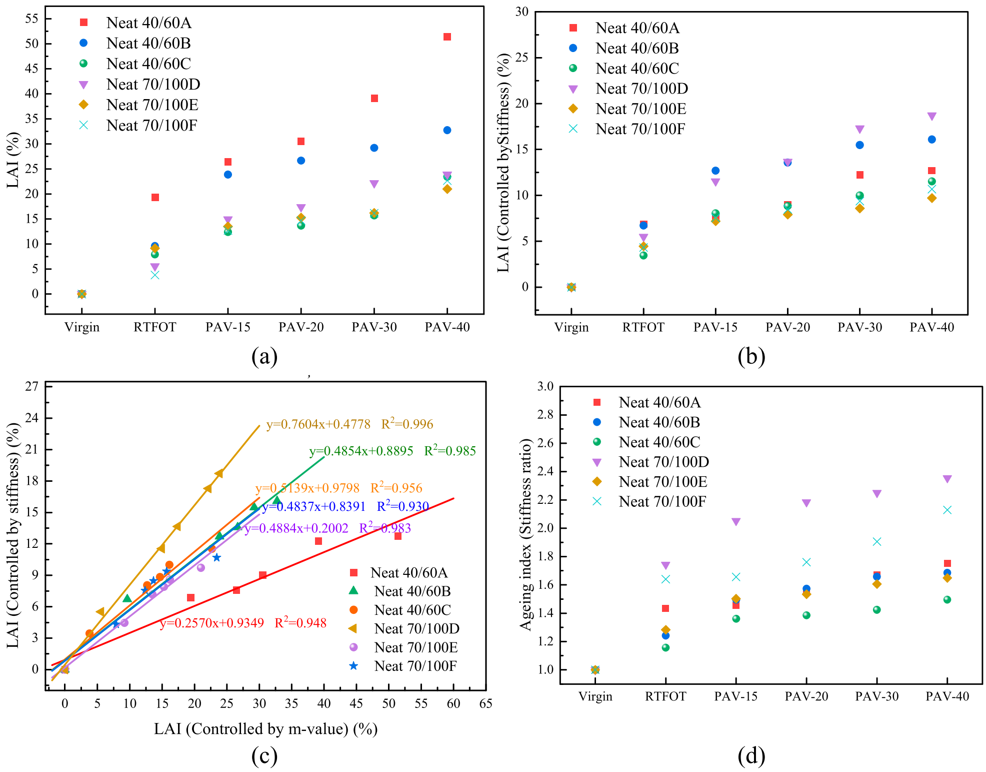

Figure 1. Low-temperature ageing indices.

two indices was carried out, as shown in Figure 1(c). It was found that the two LAIs have a strong correlation, which is denoted by the high R^2. Four of the six of the R^2 are greater than 0.95, meaning that these indices coordinate well with each other.

It is also suggested previously that the ratio of stiffness at the 60 s after and before ageing could be used to illustrate the ageing situation of bitumen. To simplify the calculation of ageing degrees based on the stiffness, the −12°C was selected as the reference temperature. It can be seen from Figure 1(d) that short-term ageing plays a dominant or comparable role compared with long-term ageing in the low-temperature performance of bitumen, which does not make too much sense. It is not surprising since stiffness is changeable upon the temperature, which limits its accuracy in characterising the ageing degrees of bitumen. If the reference temperature is being changed, this stiffness ratio-based ageing index will change accordingly, and maybe other results will be observed. Therefore, a single stiffness should avoid being employed to illustrate the ageing degrees of bitumen. However, the ageing indices based on critical temperatures are proved to be capable to characterise the ageing situation of bitumen since they are more comprehensive, as they could denote the potential thermal cracking temperatures of binders, as well as incorporating both stiffness modulus and *m*-value.

3.2. Intermediate-temperature rheological performance evaluation

The intermediate-temperature performance of bitumen, also known as fatigue or damage tolerance performance, is generally used to characterise the repetitive loading resistance ability of bituminous binders during its long-term service period. Typically, the Strategic Highway Research Program (SHRP) is proposed to use the fatigue parameter ($|G*|\sin\delta$) to characterise the fatigue resistance of bituminous

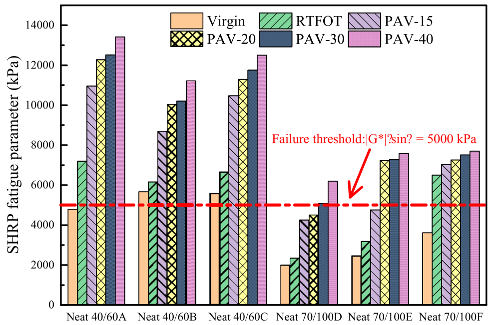

Figure 2. Superpave fatigue parameter of binders in different ageing situations.

binders (Anderson & Kennedy, 1993). However, this parameter is struggling to evaluate the actual anti-fatigue performance of some binders, especially for the modified binders and it is a poor surrogate for cracking performance (Bahia et al., 1999, 2001). The recently proposed *G-R* parameter is one of the most acceptable indices to be closely related to the damage tolerance properties of most kinds of binders (Rowe et al., 2014). The *G-R* parameter is expressed as $[|G*|\cos^2\delta/\sin\delta]$ and it is based on the LVE principal, which is the same as Superpave fatigue parameter. A higher value of *G-R* parameter means the more brittle of the materials and thereby the poorer cracking resistant. The fatigue parameters calculated by Superpave method and *G-R* parameter are plotted in Figures 2 and 3, respectively. The data were obtained from the frequency sweep and subsequently master curves were built by a 2S2P1D model (Di Benedetto et al., 2004, 2007; Olard & Di Benedetto, 2003).

It can be seen from Figure 2 that ageing plays a key role in the evaluation index of Superpave fatigue parameter of binders. It is required that the fatigue parameter should not exceed 5000 kPa or it will fail the criteria. Lower fatigue parameter stands for better fatigue resistance. Short-term ageing causes a slighter deterioration of the fatigue resistance compared with long-term ageing. The longer the ageing lasting, the more serious of the deterioration of fatigue resistance. It is noteworthy that the Superpave fatigue parameter is reported to have poor correlation with the actual fatigue damage situation of asphalt mixtures and pavement. The above drawn conclusions could be utilised to illustrate and compare the effect of ageing on the fatigue resistance of binders to some extent while it is not eligible for justifying the actual fatigue damage of binders as reported before. *G-R* parameter was proved to have a close correlation with the fatigue performance of asphalt pavement. Generally, the *G-R* parameter is calculated using the norm of complex moduli and phase angles measured or shifted from master curves at 15°C and 0.005 rad/s. There are two critical limits for *G-R* parameter: the 180 kPa is regarded as the onset point of fatigue failure and 450 kPa is regarded as the significant propagation point of failure. The *G-R* parameters for different binders in terms of ageing are plotted in Figure 3.

It was found from Figure 3 that short-term ageing slightly increases the *G-R* parameter, which is almost neglectable. Long-term ageing is very harmful to the fatigue resistance of binders and the longer ageing period contributes more to the deterioration of fatigue performance of binders. This conclusion really aligns with that obtained from the Superpave fatigue parameter. All softer binders met the criteria though ageing higher the *G-R* parameter gradually. However, ageing takes the stiffer binders (Neat 40/60) after 20-h PAV to the damage zone, especially the Neat 40/60A binder, whose *G-R* parameter has exceeded the significant cracking propagation threshold. Since the Superpave fatigue parameter and *G-R* parameter are both LVE-based and shifted from frequency sweep, it will be useful to analyse the correlation between them, thereby to find an index to evaluate the ageing degrees of binders in terms of fatigue performance. The correlation analysis was carried on, as shown in Figure 4.

It was found that the two fatigue parameters have poor correlation, with the R^2 range from 0.19 to 0.88, which is not high enough. In accordance with previous research outcomes, the *G-R* parameter is believed to be more accurate and realistic to evaluate the fatigue performance of bituminous binders

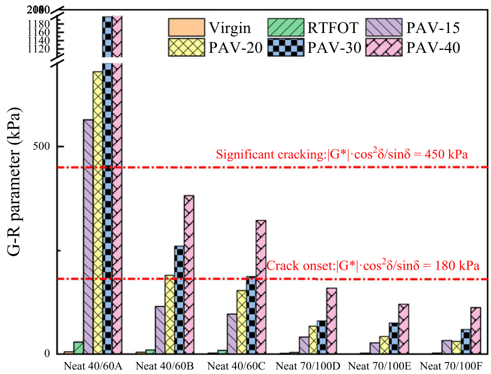

Figure 3. *G-R* parameter of binders in different ageing situations.

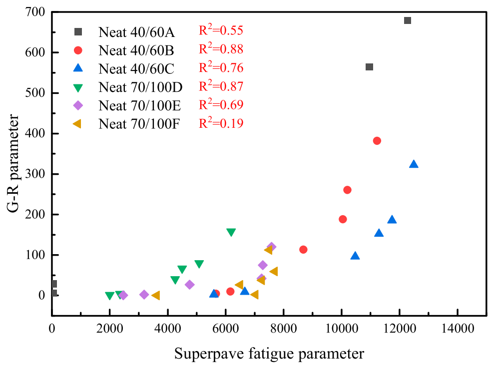

Figure 4. Correlation between Superpave fatigue parameter and *G-R* parameter.

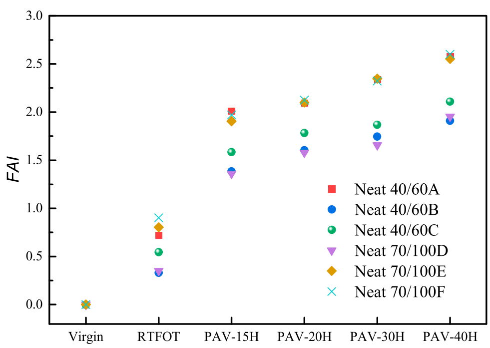

Figure 5. FAI of binders in different ageing situations.

(Wang et al., 2020). Therefore, the *G-R* parameter was employed to evaluate the ageing degrees of binders in terms of fatigue performance. The fatigue ageing index (FAI) is defined as the ratio of *G-R* parameter after and before ageing in logarithmic scale, as shown in Figure 5. It was found that the FAI shows amazing consistency with each other. Though different binders show different fatigue resistance in terms of ageing, the FAIs go almost parallelly, indicating that ageing has similar impact on the fatigue resistance of binders. Therefore, this index is strongly recommended.

Since ageing-leaded cracking is the main issue of bitumen, the thermal cracking and fatigue cracking were compared in Figure 6. The dashed lines represent the cracking-warning values, and the solid

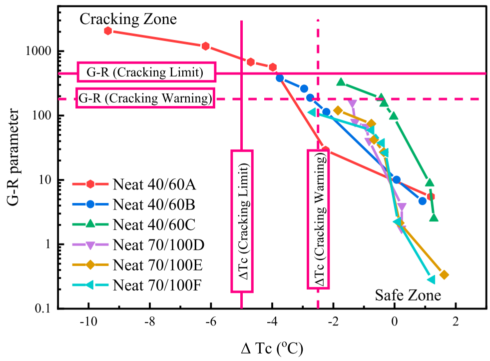

Figure 6. Cracking criteria of different methods.

lines represent the cracking-limit values for the two parameters of ΔTc and *G-R*. Points in the bottom right quadrant of the plot are acceptable under both criteria whereas those in the top left quadrant would be sensitive to cracking using both criteria. The virgin and short-term conditioned binders generally fall into the safe zone, which means that typically no cracking problems are expected. With ageing, they move toward the upper left quadrant, indicating that there may be significant cracking problems (Airey et al., 2022). It is also captured that ageing causes more cracking sensibility to stiffer binders than softer binders. Also, it is observed that elastomeric binders are known to perform better with respect to cracking often have low values of ΔT_c. Moreover, ageing has more significant influence on the fatigue aspects of binders than thermal aspect by the means of cracking.

3.3. High-temperature rheological performance evaluation

The MSCR is regarded as the best available test to estimate the high-temperature performance of bituminous materials. There are two output parameters: the nonrecoverable creep compliance (J_{nr}) which stands for the rutting susceptibility and the percent recovery (%*R*) which is responsible for the elastic response and stress dependence of binders (Liu et al., 2021). Figure 7 is the schematic of MSCR curves. Significantly, ageing reduces the strain of bitumen, leading to a better deformation resistance. The severer the ageing, the better the rutting resistance. Even short-term ageing causes a considerable reduction of strain while different long-term ageing lasting periods have slight differences.

The J_{nr} and %*R* are summarised in Figure 8. The column charts in Figure 8 are related to the J_{nr} and the scatter charts are related to %*R*.

It is illustrated from Figure 8(a) that the value of J_{nr} of bitumen decreases continuously with the ongoing of ageing. These results are expected due to the hardening of binders caused by ageing. After the short-term ageing, the value of J_{nr} drops dramatically, followed by another sharp dropping caused by 15-h long-term ageing. However, within the different long-term ageing, though the J_{nr} keeps decreasing, the downtrend becomes obviously insignificant. The change of heavy fractions is responsible for these phenomena. After the effect of oxidation, especially at a high temperature and pressure, the heavy fractions such as asphaltene tend to be a stable equilibrium, as detected by gel permeation chromatography previously (Cuciniello et al., 2021). However, slight change in the polarity and the molecular still occurs. When it comes to the J_{nr} at 3.2 kPa, the J_{nr} of binders show the same trend as that at 0.1 kPa, which decreases rapidly between the virgin situation, short-term aged situation, and long-term aged situation. For the first decline, it is caused by the volatilisation of the light components due to high temperature, which significantly hardens the binders. For the second decline, it is caused mainly by the thermal oxidation of binders, in this case, there are complex interactions

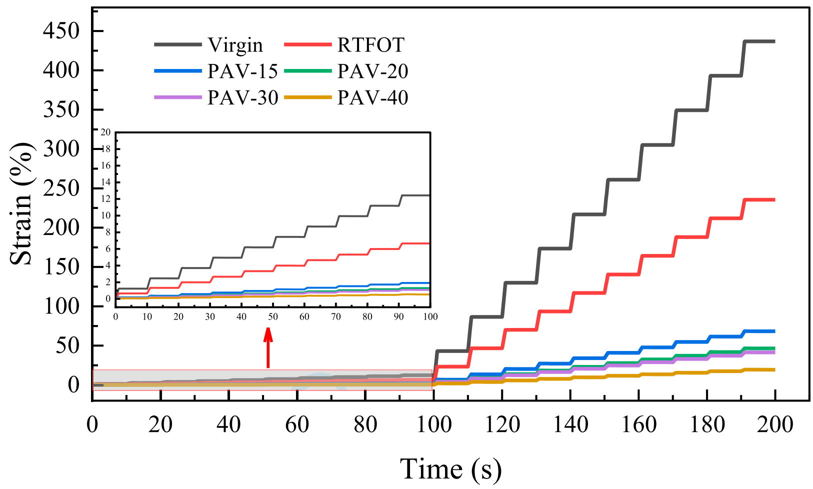

Figure 7. Schematic of MSCR curves of bitumen in terms of ageing.

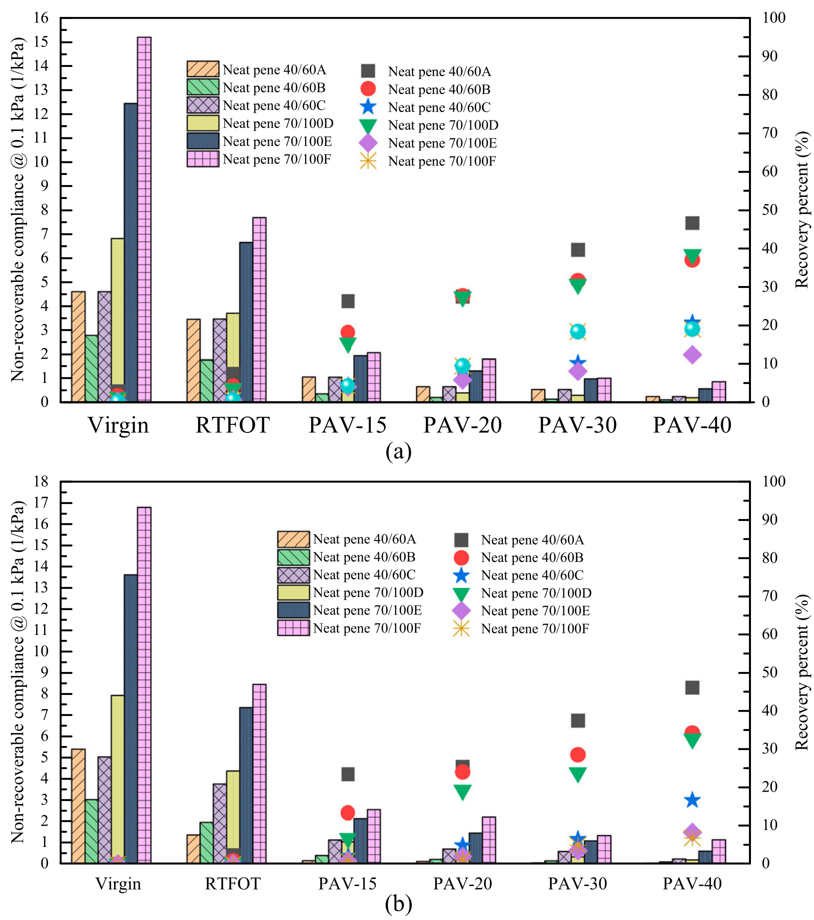

Figure 8. J_{nr} and %*R* of binders in terms of ageing situations.

within the bitumen, the light components such as saturates and aromatics transfer to heavy components such as resins and asphaltenes, thereby hardening the bitumen again. Finally, the bitumen prior to forming a relatively stable phase leads to the very slight deterioration of J_{nr}.

For the recovery percent at 0.1 kPa, the bitumen tends to have a better recoverability with ageing. At the testing temperature (64°C), the virgin bitumen is dominated by their viscous components, which almost does not have any recoverability. With the ongoing of ageing, the binders tend to be more elastic, and therefore the %R is increasing. For the %R at 3.2 kPa, the bitumen shows the same behaviour as that as 0.1 kPa, which increases gradually with ageing ongoing because of the hardening of binders.

To investigate the stress sensitivity of binders in different ageing situations, the $J_{nr-\text{slope}}$ parameter, as defined in Equation (5) (Stempihar et al., 2018), is employed.

$$J_{nr\text{ - slope}} = \frac{J_{nr3.2} - J_{nr0.1}}{3.2 - 0.1} \times 100. \tag{5}$$

To quantificationally characterise the ageing level of bitumen in terms of the high-temperature performance, the high-temperature ageing index (HAI) was proposed as per Equation (6). It is known that smaller J_{nr} and $J_{nr-\text{slope}}$ are always favourable because the former means better resistance to permanent deformation and the latter means better insensitivity to stress. Therefore, incorporating the $J_{nr-\text{slope}}$ into the J_{nr} can get a more comprehensive understanding of the rutting resistance of bitumen.

$$\text{HAI} = \log\left(\frac{J_{nr3.2\text{ - virgin}}}{J_{nr3.2\text{ - aged}}} \times \frac{J_{nr\text{ - slope - virgin}}}{J_{nr\text{ - slope - aged}}}\right). \tag{6}$$

It can be seen from Figure 9 that the HAI characterises the ageing behaviour in terms of high-temperature performance of bitumen efficiently. With the ageing ongoing, the HAI increases in different routes for different binders. For all binders, the most significant increasing of HAI occurs between the short-term ageing and the long-term ageing stages, indicating that long-term ageing dominates the high-temperature properties of binders. During this period, the bitumen gets harder mainly due to the oxidation, and the slight volatilisation of light portions also contributes to the hardening a little bit. Since the onset of long-term ageing, the binders prior to forming a stable equilibrium, at which stage the HAI increases relatively slower than before. It is worth mentioning that the HAI combinates the J_{nr} together with the $J_{nr-\text{slope}}$, which makes it competent for characterising the ageing resistance in terms of the high-temperature performance of bituminous binders, as well as to evaluate its stress sensitivity. The lower the HAI, the better the permanent deformation resistance and the more insensitive to stress, which is favourable. The reason why recovery percent is omitted in this index is that at the high stress, e.g. 3.2 kPa, the %R is always zero for some dedicated virgin and short-term aged binders, which makes this parameter not capable to be employed. Moreover, the J_{nr} and %R are always interlinked, a lower J_{nr} can represent a higher %R, therefore, the combination of J_{nr} and $J_{nr-\text{slope}}$ is adequate to characterise the high-temperature performance of binders in terms of ageing.

3.4. Comprehensive ageing index

The master curves can exhibit the rheological properties of binders in a whole-temperature range quantitatively. To quantify the holistic impact of ageing on the rheological properties of bitumen, the whole-temperature ageing index (WAI) was proposed, as defined in Equation (7), which is a further modification of previous works (Cavalli et al., 2018; Poulikakos et al., 2019).

$$\text{WAI} = \frac{\int_{-3}^{3} \log|G*_{\text{aged}}|\xi - \log|G^*_{\text{virgin}}|\xi \, d\xi}{\int_{-3}^{3} \log|G^*_{\text{virgin}}|\xi \, d\xi} \times 100\%, \tag{7}$$

where $|G*|$ is the norm of complex modulus and ξ is the reduced frequency.

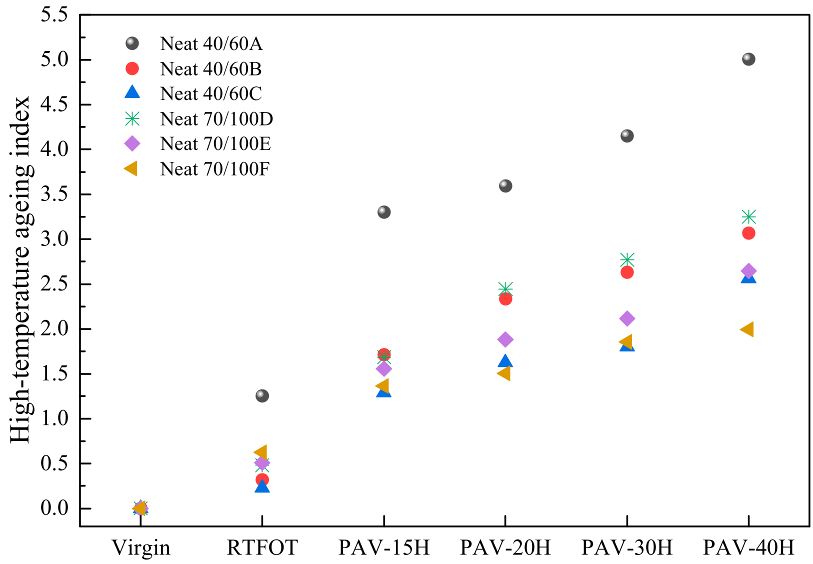

Figure 9. HAI.

In accordance with Equation (7), the WAI is the integration area differences between the master curves of the complex modulus in different ageing situations, then divided by the integration of the moduli at virgin stage, as shown in Figure 10(b). In this study, −3 and +3 were selected as the lower and upper limit, respectively, because most of the master curves fall into this range. It can be seen from Figure 10(a) that ageing leads to an increase of complex modulus which indicates that binders are getting stiffer while a decrease in phase angle which means that binders are getting more elastic.

Figure 10(a) illustrates and characterises to what extent the binders are aged based on moduli by the means of the whole master curves, which eliminates the deficiencies of using only one point to evaluate the ageing degree of binders. Generally, the binders with higher moduli (lower penetration) are prior to having higher WAI values, though the values of different binders do not have specific rules in terms of their penetration grade. It is noteworthy that the effect of ageing on rheological properties of binders seems to be nonlinear, which is indicated by the nonuniform increasement of WAI. The WAI leaps from the virgin situation to short-term ageing first, then leaps again from short-term ageing to long-term ageing, indicating that different ageing methods contribute to different ageing responses. The internal changes of the bituminous binders' components may lead to this phenomenon, and this should be determined with the aid of chemical technologies.

3.5. Chemical properties of binders in terms of ageing

The generic fractions of bitumen were measured by TLC-FID. Figure 11 is the FID signal versus retention time (the time for solute to pass through a chromatography column).

The area of each peak stands for the contents of the generic fractions of binders, as shown in detail in Figure 12.

It was found that the content of saturates decreases very slightly, which is almost the same trend with asphaltenes while in opposite manner. It is noteworthy that this is not always the case, some binders show different trends which the content of saturates keeps stable or slightly fluctuates with ageing, which may be caused by its inert nature to oxygen and the measurement error. However, it is always the case for all binders that the aromatics decrease significantly while the resins increase significantly, which means that considerable aromatics were transferred to resins, increasing the polarity of binders significantly. Though some literatures also believe that the resins are further transferred

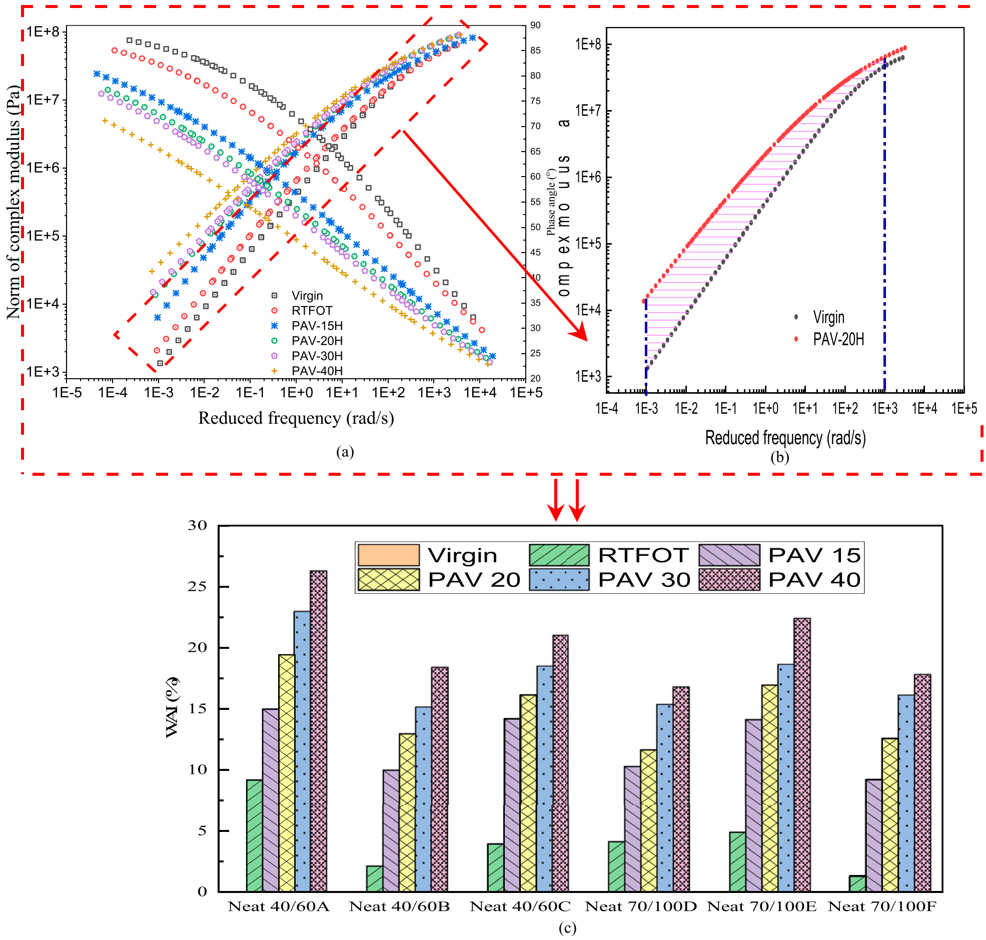

Figure 10. Calculation of the WAI: (a) master curves of binders in different ageing situations; (b) schematic of WAI; and (c) WAI for different binders at different ageing situations.

to asphaltenes, however, this trend is not significant. It is known that highly polar asphaltenes were dispersed within a lowly polar matrix, forming the 'colloidal system' (Hofko et al., 2015). The colloidal index (CI) is regarded as an ideal tool to explain the stability of this system, as defined by Equation (8) (Loeber et al., 1998).

$$CI = \frac{\text{aromatics} + \text{resins}}{\text{saturates} + \text{asphaltenes}}. \quad (8)$$

A higher CI means that the asphaltenes are more peptised by the maltene phase and the system is more stable. The CI for each binder in different ageing situations is shown in Figure 13. The naming of SARA is simply a way to categorise solubility of each component within bitumen. The generic fractions of binders were measured as per their solubility; therefore, the CI is scientifically sound and completely applicable to evaluate the colloidal stability of binders in terms of ageing (Haghshenas et al., 2022). It can be seen from Figure 13 that the CI decreases with ageing, meaning that the chemical workability of binders are gradually reduced by ageing and the colloidal system tends to be instable. It is also observed that different binders show different decreasing manner, which may be dominated by the original chemical properties of binders. The more significant the decreasing trend is, the more ageing-sensitive the binder is.

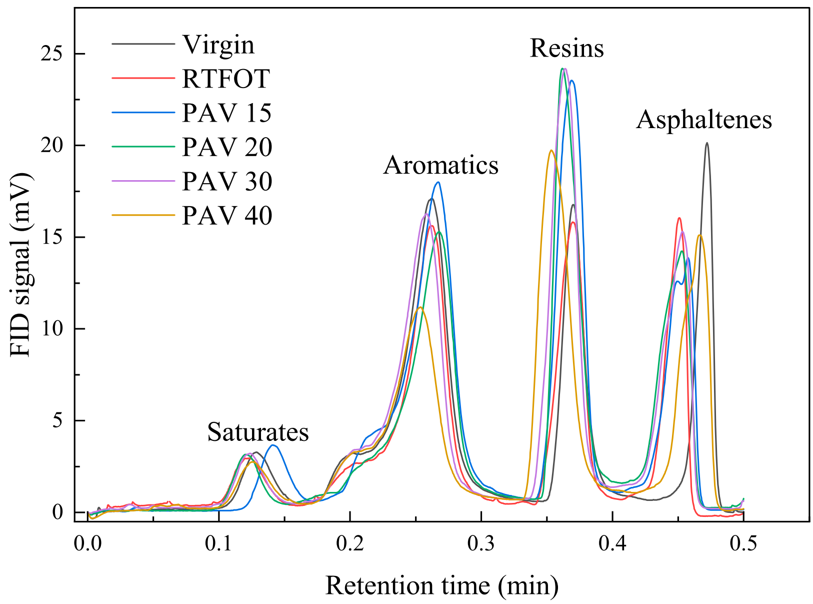

Figure 11. Generic fractions of bitumen in terms of ageing.

3.6. Correlations between chemical–rheological properties of binders

Ageing itself is a chemical process, which thereby induces the change of rheological properties of binders. To investigate how ageing changes the rheological properties of binders, the correlation analysis was performed, as shown in Figure 14. Each proposed rheological ageing indices were compared with the CI to find a link between the chemical and rheological properties of binders in terms of ageing. The correlation analysis was based on a linear empirical method because it is simple and explicit.

It is hypothesised that the ageing performance of binders is highly dependent on the chemistry and compositional properties of binders since each binder shows different correlations between chemical and rheological properties in terms of ageing. However, the correlation trends are very similar. It was found that there are strong linear correlations between the chemical-based index and rheological-based indices. Figure 14(a–d) shows the correlations between CI and low-temperature rheological ageing index, fatigue rheological ageing index, high-temperature rheological ageing index and whole-temperature range rheological ageing index, respectively. As addressed before, the rheological indices increase with ageing while the chemical index decreases with ageing, therefore an inverse correlation can be observed. There are six binders being tested in this study, from Neat 40/60A to Neat 70/100F; the penetration increasing gradually. It can be seen from Figure 13 that the CI increases with the penetration (except for Neat 40/60C, which is out of this law and may be caused by its natura property, which cannot be detected by the methods employed in this study) while decreases with ageing. It makes sense because ageing leads to the reduction of penetration. Moreover, it seems that softer binders have better colloidal stability than stiffer binders. Ignore the Neat 40/60C binder, and it was found that the slope of the fitting curve is increasing from the left-hand side to the right-hand side, meaning that for softer binders, the CI decreases slower than the increasing of rheological indices; in another words, the rheological indices are more sensitive to ageing than the colloidal stability index. Since the CI is well recognised among the industry of bituminous binder, the strong correlations between the chemical–rheological indices are solid evidence to prove that these novel rheological ageing indices make sense and are eligible for evaluating the ageing degrees of binders. However, the SARA properties are

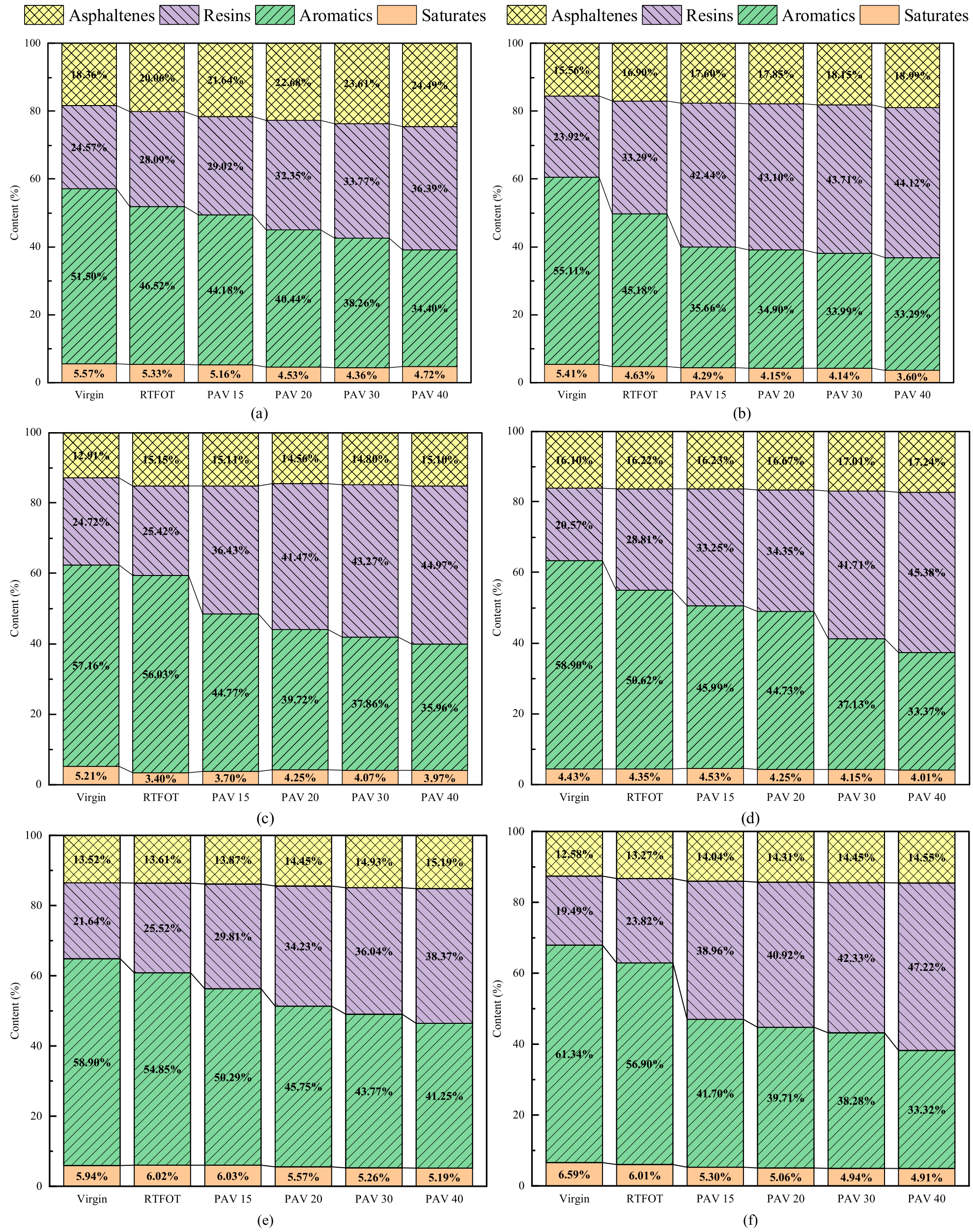

Figure 12. The change of SARA contents in terms of ageing.

a little bit rough to illustrate the chemical properties of bituminous binders, some more accurate methods such as FTIR are needed to do further investigation. These works are ongoing within the research team.

4. Summary and conclusions

To evaluate and characterise the ageing degrees of bitumen, the frequency sweep, MSCR and BBR were performed. Several rheological ageing indices were utilised or proposed to accurately characterise

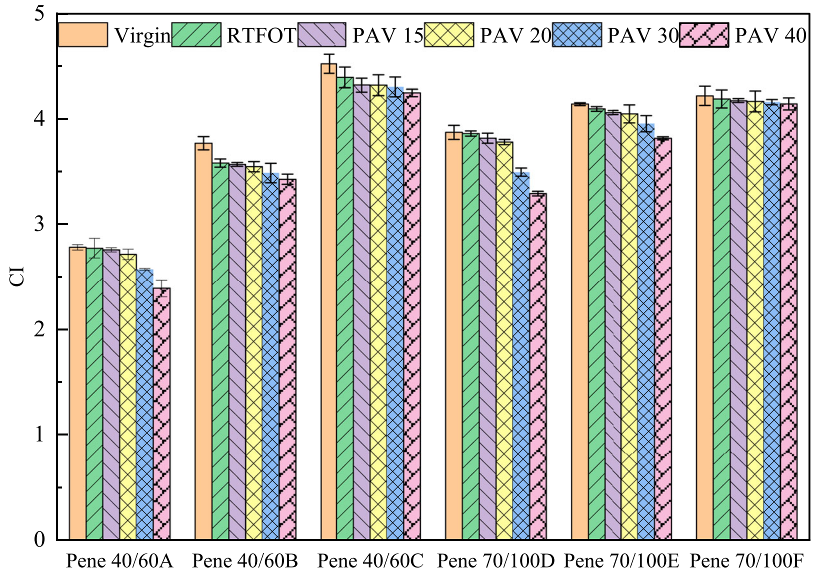

Figure 13. CI of binders in terms of ageing.

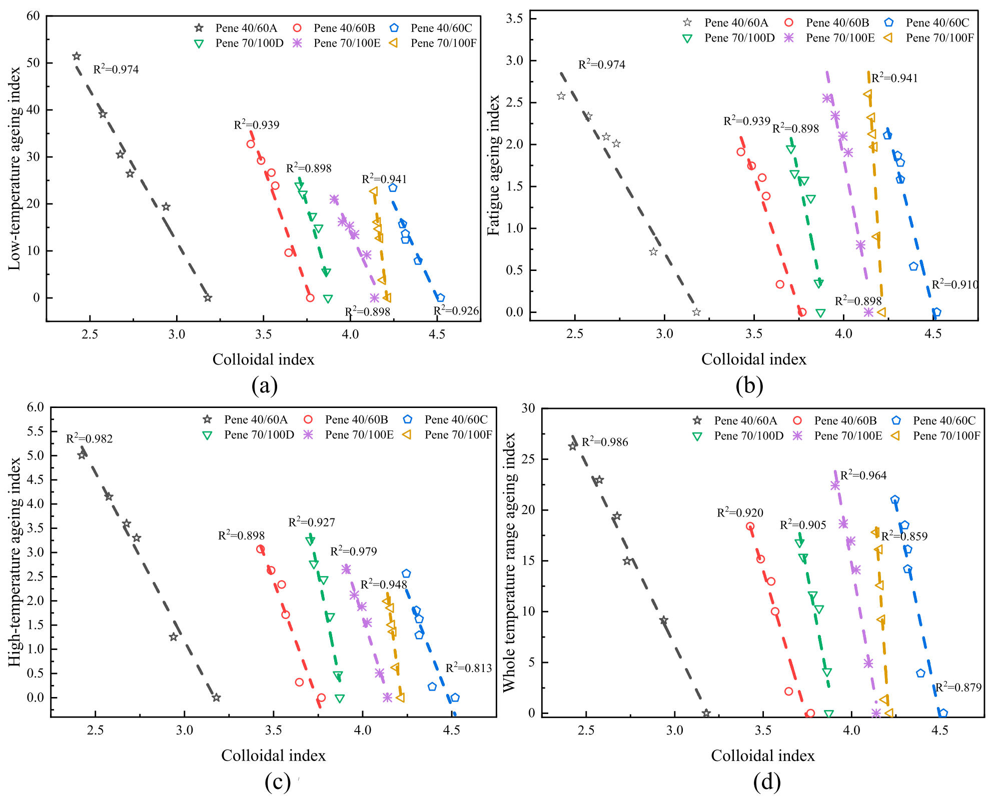

Figure 14. Correlations between chemical–rheological ageing indices.

the ageing levels of binders. Finally, the correlations between chemical ageing index and rheological indices were analysed. The following conclusions could be drawn:

- The critical temperatures controlled by *m*-value is more sensitive to ageing, indicating that the creep rate always controls the thermal cracking process, and the embrittling is responsible for the deterioration of the low-temperature performance of bitumen.
- There is a significant decline of compliance between the virgin situation and short-term ageing situation because of the volatilisation of light components, followed by another significant decline caused by long-term ageing due to the thermal oxidation of binder. However, the compliance is insignificant between different lasting periods of long-term ageing.
- Four ageing evaluation indices were proposed based on critical temperature, nonrecoverable compliance, *G-R* parameter, and moduli, which could be used to characterise the ageing degrees of bitumen in terms of its low-, intermediate-, high- and whole range temperature performance.
- There is a strong linear correlation between the chemical and rheological ageing indices, which proves that these indices are reliable to evaluate the ageing degree of bitumen.
- As per the new proposed ageing indices, assuming that the initial status for virgin binders equals to zero, the average values of LAI for tested binders for short-term aged, standard PAV and double PAV could reach to 9.24%, 19.70% and 29.19%, respectively; for the FAI, it could be 0.61, 1.88 and 2.28, respectively, and for the HAI, it could be 0.57, 2.23 and 3.09, respectively.

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