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Abstract

Nowadays, Reclaimed Asphalt (RA) is widely used in pavement applications as part of new asphalt mixtures. To design high-quality asphalt mixes, the RA material and especially the RA binder must be systematically characterised with the purpose to explore its ageing state, especially when RA is added in high rates (above 20%). In this research, chemical (SARA and FTIR ageing indexes) and rheological properties (master curve parameters, Glower-Rowe parameter and ΔT_c) of a large selection of RA binders (19 samples) were determined to reveal their ageing level. The results of this experimental validation were further analysed statistically to discover clusters of similar chemo-rheological properties, reflecting in this way their ageing state. The exploratory techniques PCA and HCA were able to detect five clusters of RA binders with different ageing states. The five clusters clearly distinguish the RA binders in groups with statistically different properties, assessed using one-way ANOVA. The method proposed here is a potential tool to "fingerprint" RA binders with similar ageing states, particularly for decision-making strategies, to optimise the use and treatment of RA.

Highlights:

- A large selection of RA binders was chemically and rheologically tested.
- Ageing states can be distinguished based on HCA and PCA analyses.
- RA binders showing similar basic properties differ in terms of their ageing state.

Keywords: reclaimed asphalt; asphalt binder ageing; clustering analysis; ageing states; bitumen relaxation;

1. Introduction

When a flexible pavement reaches its end-of-life point, the asphaltic layers can be milled and recycled in new asphalt mixtures. The material derived from the milling process is labelled as Reclaimed Asphalt (RA). In the road construction sector, RA induces considerable economic and ecological benefits [1, 2]. In order to ensure the high performance of the mixture, essential steps must be considered for the comprehensive characterisation of the

components and most importantly, the RA material. Previous studies have demonstrated that adding RA can strongly influence the mechanical properties, primarily when RA is utilised in higher percentages [3, 4].

In practice, RA is collected from different asphalt sources and layers with different original properties and specifications. In Flanders, asphalt plants collect and classify the RA material according to the asphalt and aggregate particle size distribution ("black" and "white" curve) and the penetration value of the recovered binder. Based on those properties, RA is piled providing "homogeneous" RA material for future use, aiming to reduce variability. The size of the site and the strategies for each asphalt plant can influence the number of piles and thus create less or more homogeneously grouped material. The suitability of a RA binder is reflected by the penetration value; according to the Flemish procurement regulations for road construction SB250 v3.1, RA binders with pen lower of 10 are not permitted to be reused in new asphalt mixtures, since they are considered as extremely aged [5]. Yet, penetration will not adequately capture other factors such as the crude oil source of bitumen, modification presence and more importantly, its ageing history [6, 7].

When it comes to the performance characterisation, hitherto many researchers have investigated the changes in physical, chemical and rheological properties that asphalt binders undergo during ageing. Bitumen chemistry can unravel an undesirable effect called oxidative ageing of bitumen [8]. It is widely accepted that the severity of ageing can be tracked by capturing the change in particular functional groups such as the sulfoxides and carbonyls [9-12]. From the newly formed compounds, carbonyls and carboxylic acids are of high polarity, having strong associations with other active polar sites in the binder, as expressed through their Van der Waals forces. These polar compounds of bitumen interact with each other, in some cases, reasonably strong [12]. This contributes towards increasing the polar-polar interactions, leading eventually to an increment in viscosity. It is also accepted that an increase in apparent molecular weight reduces the mobility of molecules to flow, which eventually will influence bitumen rheology [10, 11, 13].

Moreover, bitumen can be characterised based on its solubility, which is affected by the size and polarity of organic molecules, into four fractions: Saturates, Aromatics, Resins and Asphaltenes (SARA). The first three fractions, i.e. Saturates, Aromatics and Resins, form a broader group, the Maltenes. In terms of bitumen ageing, SARA classification allows for the quantification of the chemical changes in the bituminous binder, due to a sequential reaction of aromatic to resin and finally to asphaltenes. Among these fractions, asphaltenes are characterised by more polar molecular interactions, and they are considered as the principal responsible factor for viscosity increase [8].

For the evaluation of the ageing process, specific criteria have been established to compare the extent of ageing and predict to some extent, the related distresses. Previously, many studies have focused on the relationship between oxidative ageing and alterations in physical properties of bitumen such as penetration, softening point, viscosity, ductility and stiffness [14, 15]. In asphalt, the change of these properties can be related to adhesive and cohesive bond strength with the mineral skeleton and lead eventually to cracking and ravelling. Bitumen is one of the determining factors for asphalt pavement's durability and long-life performance; therefore, high oxidative ageing of asphalt binders leads to limited service life of the asphalt mixture. Ageing causes stiffening and brittleness of the bitumen, translated by an increase of complex modulus (G*) and a decrease of phase angle (δ) [14], consequently leading to changes in the asphalt mixture performance, such as fatigue resistance [16].

Although major research focused on RA binders, has been confined to the determination of the aforementioned physicochemical properties upon ageing, it still cannot reveal their ageing history without prior knowledge of the properties during their original unaged state. Therefore, more extensive chemical and rheological characterisation is essential to unravel information that can be linked to the extent of ageing of the asphalt binders. In this paper, RA binders are evaluated and grouped according to their ageing severity, which from hereafter is defined as ageing state, based on the chemical and rheological properties of the binder's current condition.

A promising technique to approach the analysis of chemo-rheological properties is by using exploratory statistical methods to detect patterns among the studied samples, based on similarities between the input data. Among typical methods to detect such pattern structures are the Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA). This approach is well-reported and applied in other fields, namely in food

sciences [17, 18], in geochemistry studies [19] and physics [20]. In bitumen-related studies, Wang et al. have successfully explored differences on asphalt binders manufacturers, using PCA on FTIR data [21]. In a similar study, Ren et al. have classified asphalt binders derived from different crude oils using the same analytical approach [22]. To the best of authors' knowledge, the abovementioned analyses have not been used previously to assess differences in ageing of bituminous samples.

The objectives of this study are first to show the diversity in properties (chemical and rheological) between different RA materials, secondly to assess the capability of penetration as a parameter to evaluate the ageing of the RA binders and thirdly to classify the RA samples into clusters belonging into similar ageing states, on a chemo-rheological basis.

2. Materials and methods

In total, 19 different RA binder samples have been collected for this research. Those samples were collected from 4 different asphalt plants from the wider area of the Flemish region in Belgium:

- samples RA1 to RA7 collected from plant A
- samples RA8 to RA15, and RA18 collected from plant B
- samples RA16 and RA17 collected from plant C
- sample RA19 collected from plant D

For each RA binder sample, a sealed cup was collected with approximately 40 grams of extracted and recovered binder. All samples were extracted and recovered by the asphalt plants (according to EN 12697-1:2012), as part of their classification process, and delivered afterwards to our laboratory for further analyses. Two types of solvents were used for the extraction, dichloromethane and trichloroethylene. The samples were first homogenised before testing. We performed penetration (EN 1426:2015) and softening point (EN 1427:2015) tests on the samples, and the results are presented in Figure 1. Three out of nineteen RA binders (samples RA8, RA11 and RA12), were found to contain traces of SBS (Styrene-Butadiene-Styrene) modification. The procedure to determine the modification presence is further explained in §2.3.

In the first stage of this research, all collected asphalt binders were subjected to a series of chemical and rheological tests and then the experimentally defined data were further analysed by means of PCA and HCA. A flowchart of the applied methodology is presented in Figure 2.

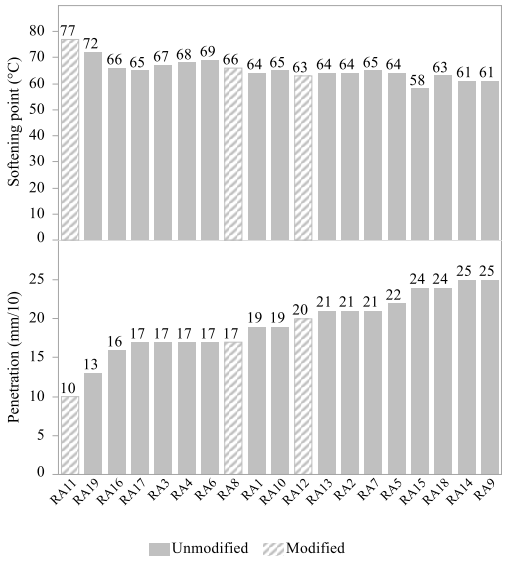


Figure 1: Penetration and softening point of the RA binders.

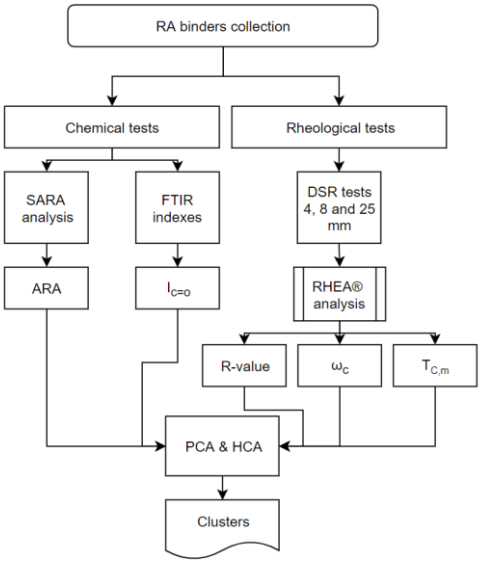


Figure 2: Flowchart of the applied methodology.

2.1. Rheological properties

To determine the rheological properties of the asphalt binders, frequency sweeps were conducted for a temperature range from – 30 to +70 °C. The asphalt binders having SBS traces were tested till +100 °C to assess the activity of SBS modification further. Two devices were utilised to cover two temperature test ranges. From – 30 till 0 °C (temperature increments of 6 °C), an Anton Paar™ MCR 101 was used to perform 4-mm tests, based on procedures described in [23, 24]. From 0 till 70 °C (temperature increments of 10 °C), an Anton Paar™ MCR 500 was used for 8- and 25-mm tests, according to EN 14770:2012. The tests were performed under strain control, within the Linear Viscoelastic Region (LVR) of the samples, at a frequency sweep from 0.1 to 10 Hz. After performing strain sweeps to determine the LVR, it was found that for all samples a suitable, non-damaging, strain level was 0.02% for the 4-mm and 8-mm setup and 0.05 % for the 25-mm geometry.

The DSR results were processed using the rheological software RHEA™, developed by Abatech Engineering Consultants [25]. The raw data are used as input for the software, and the software can generate the master curve. For the construction of the master curve, the Christensen-Andersen (CA) mathematical model was used on the shifted data [26, 27]. The software is using by default the Gordon and Shaw (G&S) shifting procedure [28]. The CA model describes the complex shear modulus (equation 1) in relation to the Glassy modulus (Gg), the rheological shape parameter (R) and the crossover frequency (ω_c) for every test frequency (ω). The shape parameter (R) can also be expressed as the difference between the log of glassy modulus and crossover modulus (where G'=G"=G_C). All data, derived from – 30 to +70 °C DSR tests, were shifted to a reference temperature T_0=20 °C. An example of a full master curve (based on 4-,8- and 25-mm DSR tests) generated by the RHEA software is presented in Figure 3. Due to binder amount limitations, one replicate was tested in 8- and 25-mm DSR tests and two replicates in 4 mm DSR tests, for each RA binder sample.

Another promising rheological parameter is the Glover-Rowe (G-R) parameter, which is associated with fatigue cracking [29]. Rowe rearranged Glover's parameter, resulting in equation 2 [30]. The G-R parameter is calculated based on the measured G* and δ at 15 °C and 0.005 rad/s. In this study, the G-R parameter was estimated from the

RHEA™ software based on the full CA master curves. Two limits have been proposed as damage thresholds: G-R = 150 kPa suggests cracking onset (warning) and G-R = 600 kPa suggests significant cracking (critical) [31]. Increased G-R values indicate more brittle asphalt binders, susceptible to fatigue cracking, as demonstrated elsewhere [32, 33].

$$G^*(\omega) = G_g * \left[1 + \frac{\omega_c}{\omega}^{(log2/R)}\right]^{-R/log2} \quad (1)$$

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

The 4-mm DSR data were used to cover the high frequency-low temperature part of the master curve when approaching the glassy modulus. Another parameter estimated by the 4-mm DSR measurements was the low-temperature rheological parameters, more specifically the relaxation parameter m-value and the creep stiffness S(t). In previous studies, the use of 4-mm DSR tests has been demonstrated as an alternative of the Bending Beam Rheometer (BBR) test [34, 35]. The advantage of the former is that it requires a smaller bitumen amount: 25 mg instead of 15 gram per replicate.

ΔTc is the difference between two lower continuous grading temperatures (equation 3), as proposed by ASTM D7643-16. When performing BBR tests, first the continuous grading temperature ($T_{c,S}$) is defined when S(60) = 300 MPa and then the continuous grading temperature ($T_{c,m}$) is defined when m(60) = 0.300. The parameter ΔT_C has been proposed by researchers as a parameter related to ageing induced cracking but also as an indicator of ageing evolution [36]. With ageing, ΔTc becomes more negative, indicating deterioration of the asphalt binders performance, making them more susceptible to cracking. Two limits have been proposed in the past as performance indicators, the limit of $\Delta T_C = -2.5$°C as a warning limit and the limit $\Delta T_C = -5$°C as a critical limit [36]. Therefore ΔT_C is a useful parameter to track the performance of asphalt pavements but also characterise reclaimed asphalt binders before use. To estimate the ΔTc parameter by DSR tests, the following conversion was applied, as proposed by MTE (Mathy Technology and Engineering) Services Inc. [34]:

- G(60) = 143 MPa instead of S(60) = 300 MPa
- m(60) = 0.275 instead of m(60) = 0.300

The calculation of the new parameters ($T_{c,G}$ and $T_{c,m}$) follows the procedure proposed in ASTM D7643-16 based on the proposed conversions. Two relaxation moduli (G_1 and G_2) and two relaxation slopes (m_1 and m_2) at two temperatures (T_1 and T_2) must be determined, where $G_1 \leq 143$ MPa $\leq G_2$ and $m_1 \leq 0.275 \leq m_2$. $T_{c,G}$ and $T_{c,m}$ are calculated based on equations 4 and 5.

$$\Delta T_c = T_{c,G} - T_{c,m} \quad (3)$$

$$T_{c,G} = T_1 + \frac{(T_1 - T_2) * (\log 143 + logG_1)}{\log G_1 - \log G_2} - 10 \quad (4)$$

$$T_{c,m} = T_1 + \frac{(T_1 - T_2) * (0.275 + m_1)}{m_1 - m_2} - 10 \quad (5)$$

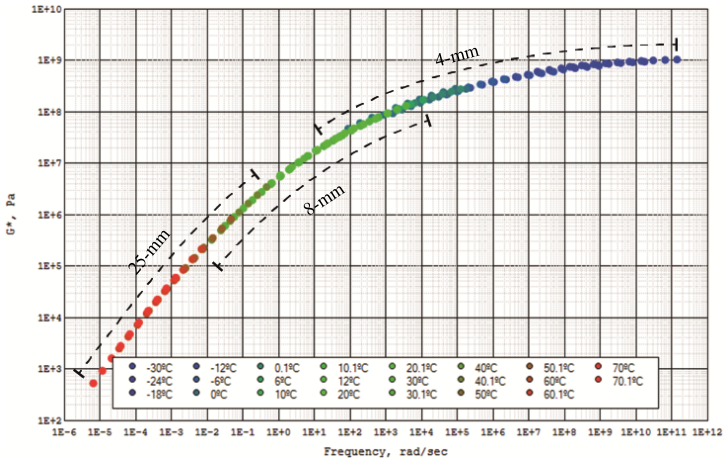


Figure 3: Example of a master curve generated from RHEA software for a temperature range between - 30 and + 70 °C.

2.2. SARA fractioning

Several methods exist to determine the SARA fractions. Typical techniques are liquid chromatographic (LC) methods, such as the recently developed method by Sakib & Bhasin [37], and the Thin Layer Chromatography-Flame Ionization Detector (TLC-FID) method. In this study the TLC-FID method was applied, making use of a IATROSCAN MK-6s, according to the protocol described in IP 469/01 [38]. This protocol can be summarised in four steps. First, dilute, bitumen dichloromethane solutions 20mg/ml are prepared. Then, the solution is applied on a silica coated quartz rod; this step is also referred to as "spotting". After spotting, the development of the sample, in different solvents takes place. For each bitumen sample, three rods were prepared. After the development of the fractions, the frame bearing 10 rods is inserted in the analyser, where the rods are sequentially passed through the flame ionisation detector (FID). A typical bitumen chromatogram consists of four peaks, where each peak represents one of the four generic fractions.

2.3. ATR-FTIR spectroscopy

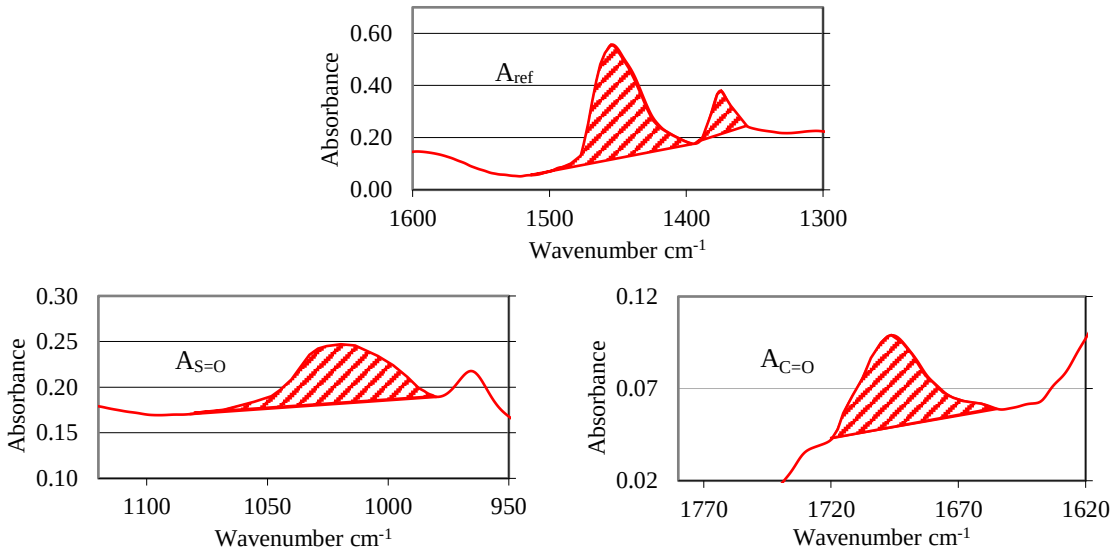
Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy is an appropriate tool to trace oxidative ageing, and namely two functional groups: carbonyls and sulfoxides [39]. For the spectra acquisition, a Thermo Scientific Nicolet iS™ 10 FT-IR Spectrometer was utilised. Every spectrum was formed as the result of 32 repetitive scans and with a resolution of 4 cm^{-1} in the range between 4000 cm^{-1} and 400 cm^{-1}.

To qualitatively inspect the presence of modification, the BRRC protocol was applied [40]. Two types of modification are available in the Flemish market, Styrene-Butadiene-Styrene (SBS) and Ethylene-Vinyl-Acetate (EVA). These modifications, when present, show typical bands in the FTIR spectrum: at 700 and 968 cm^{-1} for SBS and 1,240 and 1,740 cm^{-1} for EVA.

To quantify the ageing indexes, the procedure described by Hofko et al. [41] was adopted. The selected protocol consists of two parts. First, the spectra are normalised and then the sulfoxide ($I_{S=O}$) and carbonyl ($I_{C=O}$) indexes are calculated. The applied normalisation consists of two steps. First, a baseline correction was applied, by shifting all spectra to zero absorbance at 1753 cm^{-1}. Second, an absorbance correction factor was applied, scaling all spectra to an absorbance of 1 at 2923 cm^{-1}. For the quantification of the ageing indexes, the applied baseline limits and equations are presented in Table 1.

Table 1: Functional groups and their baseline limits used to calculate the ageing indexes.

Functional Group	Baseline Limits (cm^{-1})	Ageing Index
Aliphatic group (A_{ref})	1395-1350 1515-1395	A_{ref}
Carbonyl group ($A_{C=O}$)	1720–1665	$I_{C=O} = \frac{A_{C=O}}{A_{ref}}$
Sulfoxide group ($A_{S=O}$)	1082–980	$I_{S=O} = \frac{A_{S=O}}{A_{ref}}$



: Schematic illustration of the functional group spectra, attributed to the ageing indexes.

2.4. HCA and PCA analysis

HCA is a statistical tool that identifies clusters in the data, based on the similarities among the samples. The clustering of the samples is achieved by calculating the Euclidian distance between them, followed by stepwise clustering of the most similar variables. The result is typically depicted in a dendrogram, with shorter distances between the branches representing higher similarities between the samples. In this study, Ward's linkage criterion was selected. Both analyses were performed using the statistical software JMP® Pro 13.

PCA is an exploratory data analysis technique to represent the variation of the dataset, using a smaller number of linearly uncorrelated variables, referred to as principal components (PCs). Since the original variables may be on different measurement scales, original variables are typically centred and scaled. The standardised variables are then orthogonally transformed, so that the PCs are calculated as linear combinations of the original variables, whereby the first PC accounts for as much variance as possible, with the following PCs covering the largest possible variance that hasn't yet been covered by the preceding PCs. The number of PCs to retain is based upon how much of the variance is captured by the first PCs. Typically two PCs are retained in most cases, PC1 and PC2. In this study, the number of PCs was determined using the 80% variance criterion, meaning that the cumulative variance explained should be greater than 80%.

To detect ageing state patterns among the samples, a selection of the tested chemical and rheological parameters were selected as input variables for the PCA and HCA analyses. The selection criteria are based on two factors: firstly, the parameters should reflect the ageing evolution and secondly they should not be biased by other factors.

Various studies have reported the increase of asphaltenes and the simultaneous decrease of aromatics upon ageing. With regards to the saturates, most studies claim that they are unreactive through ageing, whereas resins can vary depending on the conditions and the crude oil [42]. Asphalt binders with lower ΔT_c suggest lower stress relaxation making them more prone to cracking, especially thermal cracking. With ageing, ΔT_c changes in an m-controlled mode [36, 43]. Therefore, to better reveal the differences between samples, the $T_{c,m}$ was incorporated in the analyses.

On the other hand, FTIR ageing indexes of RA binders can be biased, since part of the filler can remain after extraction and recovery. As a consequence this can have a big impact on the FTIR spectrum [44], especially in the case of calcareous filler which will give a signal at the approximately same band as the sulfoxide group [45], making it apparent that sulfoxide might not be an appropriate ageing indicator for RA binders. Furthermore, parameters such as the G-R parameter and $T_{c,G}$ can also indicate the ageing evolution but are also dependable to the stiffness of the virgin state of the material, which is not known. This can mislead the clustering results, since the ageing states will be driven by stiffness indicators, categorising the binders in the same, possibly false, approach that penetration does.

As a result, parameters that remain unreactive or less active throughout ageing, e.g. Saturates and $T_{c,G,}$ or can be biased by other factors, e.g. $I_{S=O}$, were not included in the analyses. The remaining parameters were evaluated as appropriate since they can be related to the ageing history but also the source (supplier, crude oil, refining process, etc.) of the binder. Finally, the selected parameters to be incorporated in the analyses are the following:

- Chemical: Aromatics, Resins, Asphaltenes from SARA and $I_{C=O}$ from FTIR analysis.
- Rheological: shape parameter R, crossover frequency ω_c from CA model and the limiting critical temperature $T_{c,m}$, all associated with binder relaxation.

3. Results and discussion

The results of this paper are divided into two parts. The first part discusses the results of the experimental evaluation of all parameters tested for the RA binders while in the second part, the results of the pattern detection analyses are presented, using as initial variables the selected parameters described in section 2.4.

3.1. Experimental evaluation

3.1.1. Rheological properties

During ageing, it is generally accepted that the complex modulus G^* of asphalt binders increases, especially at the lower time-temperature domain of the master curve, while for the higher domain they reach a plateau at approximately 1 GPa [46], the so-called glass modulus G_g. To better capture, the differences between the samples, rheological parameters of the CA model were utilised, as presented in Figure 4. In this figure, the effect of ageing on the rheological parameters is demonstrated, showing an example of an unaged penetration grade bitumen 35/50 and a RA binder. Comparing RA11 with the 35/50 bitumen, we observe a lower crossover frequency and modulus (ω_c and G_c), while the rheological index R increases. These observations are in line with findings in the literature [47, 48].

Figure 5 illustrates the master curves (experimental and fitted data) of four RA binders, RA8, RA11 and RA12 that all contain traces of SBS modification and RA2, as an example of a non-modified binder. The CA model appears to fit well for both non-modified RA binders and RA binders with SBS traces. To further assess the activity

of SBS on the samples found to contain traces, the black curves of the same selection of RA binders (as in Figure 5) are presented in Figure 6. To be able to trace any possible increased elasticity at a higher temperature, measurements were performed up to +100 °C. Comparing the RA binders with and without traces of SBS, only sample RA11 shows a small increased elasticity compared to RA8 and RA12 and therefore higher polymer activity. This observation might seem a contradictory result compared to the FTIR results that show modification presence, but the almost non-modified behaviour of RA8 and RA12 can be attributed to the effects of field ageing or also to a common practice applied by asphalt plants in Belgium. Typically, when asphaltic surface layers are milled, that commonly contain PmB binders, are subsequently mixed with base layer RA material with unmodified bitumen. The reasoning behind this practise is to avoid inserting RA material with high PmB content in the parallel drum during reheating because this could lead to material sticking on the drum's wall and with an increased risk of creating RA agglomerations, leading eventually to clogging.

The evolution of ageing can also be visualised by plotting ω_c vs R, where ageing is directed by a simultaneous increase of R and decrease of ω_c, as presented in Figure 7a [49, 50]. Figure 7b shows the space diagram ω_c vs R of the RA binders. Comparing Figure 7a and 8b, the same trend can be detected: a movement to the bottom right corner during different ageing simulations and different samples accordingly. It is evident, based on these figures, that the RA binders demonstrate different rheological responses attributed mainly to their ageing.

The G-R parameter results are illustrated in black space representation in Figure 8. Sample RA11 is positioned above the critical limit, while samples RA6, RA19, RA4 and RA16 are placed within the damage thresholds. It is expected that under consecutive ageing step simulations, a movement to the top left corner of the black space diagram will be observed, meaning that with ageing a simultaneous increase of G* with a decrease of δ is expected. The fact that the sample RA11 exhibits the highest G* and lowest δ might mean that this binder is more aged compared to the rest; however, this result can be strongly influenced also by the fact that RA11 show SBS modification traces. Practically the presence of the SBS modification will alter the rheological response of the material in high temperature-low frequency (0.005 rad/s) domains, leading to higher G* and lower δ compared to neat bitumen [51]. Therefore, the G-R parameter might be overestimated for the case of polymer modified binders. Another observation is that the RA binders follow the same trend (R^2=0.8994), as depicted by the fitted trend-line of G-R data (Figure 8). This surprising trend could be explained as if the binders "age" at the same rate. Petersen observed the same conclusion for the SHRP asphalt binders in 2009, where he supported that climate conditions influence greatly the oxidative ageing [8]. The last point supports the observation above since all the RA binders were collected from the same part of the country, where very similar climate conditions exist.

Together with the rheological parameters, the ΔT_c parameter was also determined. The ΔT_c results of the RA binders (see Figure 9) show a different trend compared to the rheological parameters. Samples RA9, RA14 and RA15 exhibit high ΔT_c indicating less aged samples, which is in agreement with the conclusion of the rheological parameters ω_c and R. However, RA binders with the lowest penetration value, that would be conventionally characterised as the most aged ones, do not exhibit the lowest ΔT_c while it is also demonstrated that ageing leads to lower ΔT_c. A possible explanation here might be the starting point (unaged state) and the service years of the binder samples, where RA11 (10 mm/10) could have been a stiffer binder compared to RA8 (17 mm/10 & highest ΔT_c) during their virgin state and/or the former was for a shorter period of time in service compared to the latter.

One should note here that only the master curve and the rheological parameters, cannot independently reveal the ageing state. A direct conclusion concerning their ageing state could effectively be drawn only in the case that all the RA binders have the same starting point, meaning similar properties in their virgin state. This highlights the necessity to consider both rheological and chemical indicators to reflect the current ageing state better.

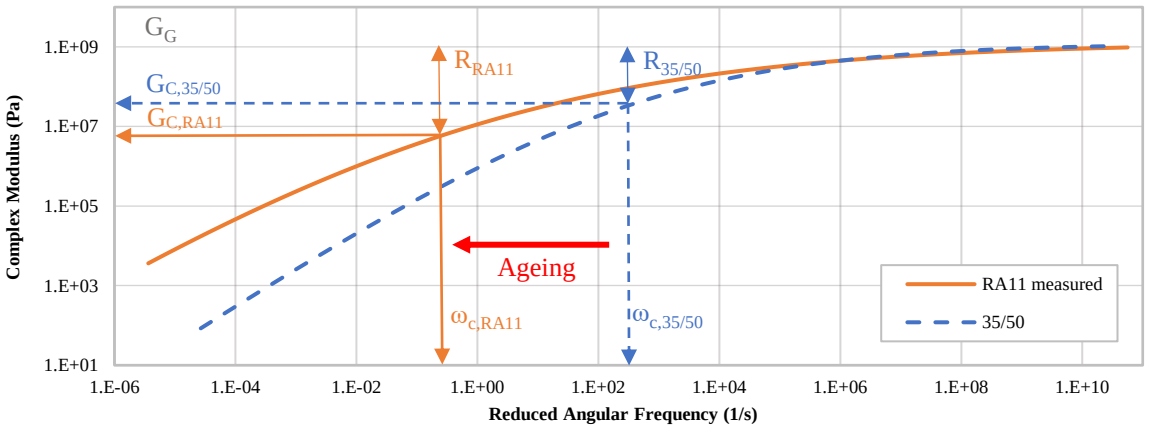


Figure 4: Evolution of rheological parameters (ω_c, R and G_c) with ageing; an example of unaged bitumen (35/50 pen grade) and RA binder.

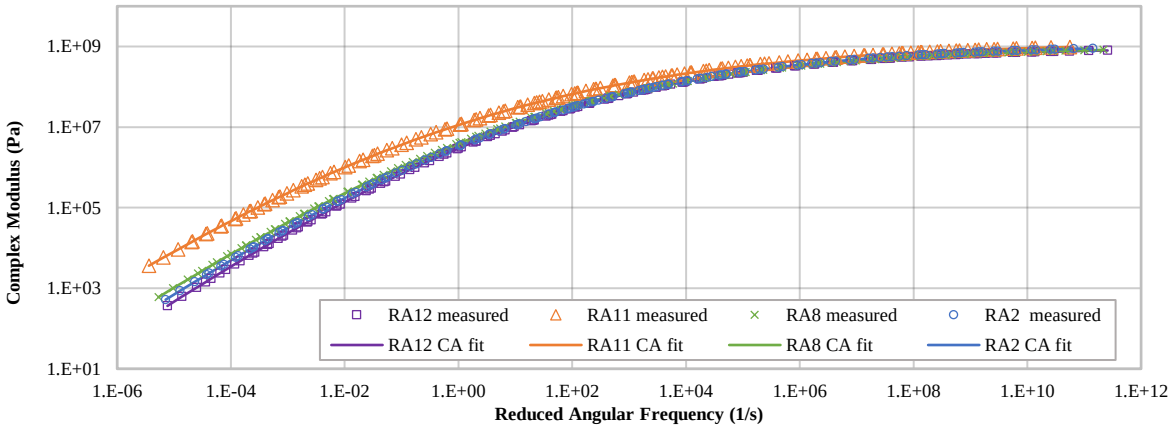


Figure 5: CA master curve of RA binders found to contain SBS traces (RA8, RA11 and RA12) and of one non-modified RA binder (RA2).

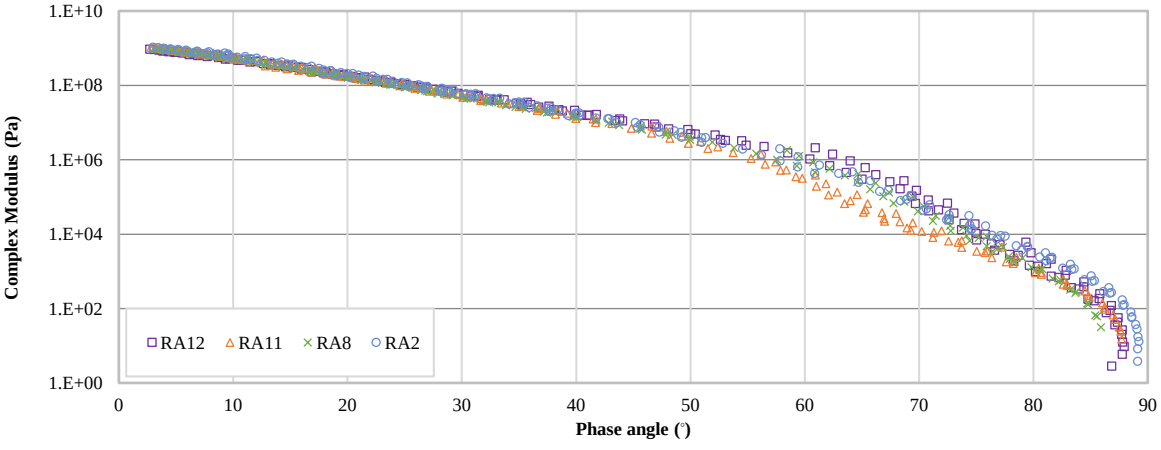


Figure 6: Black curve diagrams of RA binders found to contain SBS traces (RA8, RA11 and RA12) and of one non-modified RA binder (RA2).

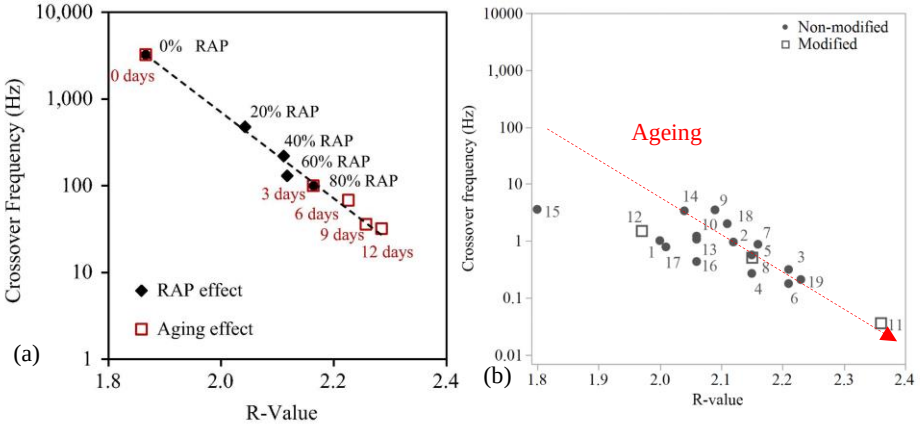


Figure 7: Effect of ageing on the evolution of ω_C vs R, based on literature [50] (a), the evolution of ω_C vs R for the different RA binders (b).

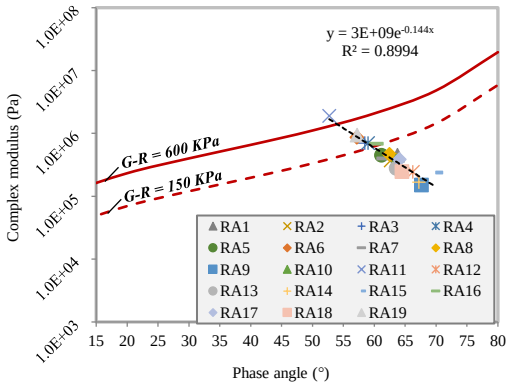


Figure 8: Representation of the G^* and δ of the G-R parameter in black space diagram, for the various RA binders.

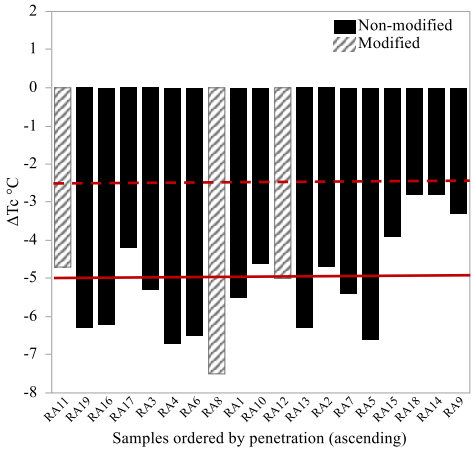


Figure 9: ΔT_C parameter of the RA binders

3.1.2. Chemical properties

The RA binders were chemically evaluated in terms of SARA fractionation, carbonyl and sulfoxide indexes. The SARA fractions were quantified using the TLC-FID method. Figure 10 presents the results of the RA samples. The first observation is that among all samples, saturates remain stable (5.55 % ± 0.73 %), which corresponds to the view that saturates remain inactive during ageing [42]. The rest of the fractions show a considerable variation among the samples showing the following trend: stiffer binders show lower aromatics and higher resins, which can be attributed to the expected transformation of aromatics to resins upon oxidation. The asphaltenes do not show any distinguishable trend. The differences between the SARA fractions could also be credited to different binder sources, derived from different crude oils and/or under different refining processes.

An additional tool that has been proved able to trace ageing is the evolution of certain functional groups using FTIR spectroscopy, namely carbonyl and sulfoxide groups. In Figure 11a, the results of $I_{C=O}$ and $I_{S=O}$ indexes are presented. Samples RA6, 11 and 19 show the highest $I_{C=O}$ values, where samples RA13 and 19 the highest $I_{S=O}$. As can be seen from Figure 11b, a trend can be observed ($R^2 = 0.560$) between $I_{C=O}$ and the rheological parameters of the master curve.

On the other hand, $I_{S=O}$ seems to be uncorrelated ($R^2 = 0.061$) for this set of data. There is widespread empirical evidence that carbonyls have shown a good correlation with the viscosity increase during long-term oxidation in contrary to sulfoxides that appeared to demonstrate weak correlation [52, 53]. A possible explanation of this weak association can be attributed to the presence of calcareous filler leftovers after the extraction and recovery process, biasing the band quantification at 1030cm^{-1}, which is the same for the sulfoxides and the filler [45].

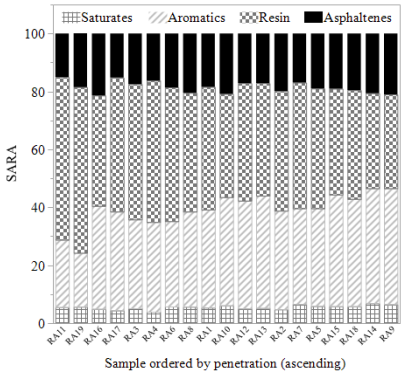
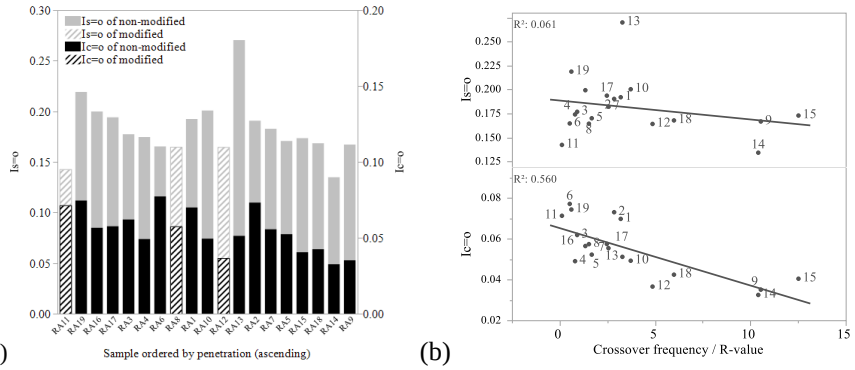


Figure 10: SARA fractions of RA binders



(a) (b)

Figure 11: Carbonyl and Sulfoxide index of RA binders (a), correlation of Carbonyl and Sulfoxide index against the ratio of Crossover frequency over R-value (combined effect)

3.2. Pattern detection analysis

To visualise subgroups in the data and to detect ageing state patterns based on chemo-rheological similarities, two exploratory multivariate data analysis techniques were applied, including Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA).

HCA calculates the multidimensional Euclidian distances, between the observations, starting from the initial variables. In this study, as input variables were considered only the selected parameters, described in the methods section (§2.4). Using a stepwise algorithm (Ward's linkage criterion), observations behaving similarly across the initial variables are linked, and the results are graphically shown in a clustering tree (dendrogram). To determine the clusters, groups of observations behaving similarly, a cut-off point must be selected.

Based on visual inspection of the derived dendrogram and the selected cut-off point (see Figure 12), the RA samples can cluster in 5 subgroups:

- Cluster 1: samples RA9, 14 and 15
- Cluster 2: samples RA10,12,13 and 18
- Cluster 3: samples RA1, 2, 5, 6, 8 and 16
- Cluster 4: samples RA3, 7. 4 and 17
- Cluster 5: samples RA11 and 19

PCA starts from the correlation between the initial variables (selection of parameters presented in §2.4), and represents the variation of the dataset, using a reduced number of linearly uncorrelated variables, referred to as principal components (PCs) [54]. PCs are calculated as linear combinations of the original variables. Table 2 contains the coefficients (the "loadings") through which the PCs are calculated based upon the initial variables. Observations with a strongly positive PC1 value have high values of Resin, $T_{c,m}$, $I_{C=O}$ and R, and low values of ω_c and aromatics. Whereas a sample with a strongly positive value for PC2 will have a high value for asphaltenes. The PCs are constructed in such a way that the first PC, i.e. PC1, accounts for as much variance as possible, with the following PCs covering the largest possible variance that hasn't yet been covered by the preceding PCs.

In the current dataset, PC1 explains 70.5 % and PC2 12.5 % of the total variance of the dataset, with the cumulative variance explained by PC1 and PC2 reaching 83 %, meeting the 80% variance criterion. Figure 13a represents the plot of the PC1 score versus the PC2 score, which illustrates the position of the samples in a new coordinate system formed by PC1 and PC2. In Figure 13b each arrow represents an original variable, and the correlation between two original variables is proportional to the cosine of the angle between them. Table 2 presents the factor loadings of both PCs. More specifically, PC1 is positively correlated with Resin, $I_{C=O}$, R and $T_{c,m}$ while negatively correlated with aromatics and ω_c. PC2 is negatively correlated only with Asphaltenes.

Based on the score plot we can conclude that the clusters 1, 2 and 3 are driven by PC1, cluster 1 and 2 in the low positive side of PC1 and cluster 3 in the high positive, where high values for Resins, $I_{C=O}$, R and $T_{c,m}$ result in a strongly positive value of PC1. On the other hand, cluster 4 and 5 are characterised by negative PC1 values, which is driven by high values of aromatics and ω_c, which have negative loadings on PC1. PC1 explains the more substantial part of the data variance (70.5 %) showing high loadings for most of the inserted factors (except the asphaltenes).In line with this observation, 4 out of 5 clusters can be distinguished based on PC1.

Although the HCA dendrogram suggests that cluster 1 and 2, as well as cluster 4 and 5 could be merged if a higher cut-off would be selected, the PCA score plot shows a clear distinction between the 4 clusters. Cluster 1 and 2 are separated mainly by their PC2 score. Since asphaltenes show a strong loading on PC2, this implies that cluster 1 and 2 differ in asphaltenes, whereas clusters 4 and 5 differ by their PC1 score, which is driven by high aromatics and ω_c. This observation enables a better interpretation of the results and the underlying structure of the clusters.

Using one-way ANOVA (Analysis of Variance), we determined which of the original parameters incorporated in the HCA and PCA analysis differ between the clusters. Across all parameters inserted in the PCA and HCA, we observe a significantly different mean value between the clusters (p-value < 0.05). Mean values for each parameter within the 5 clusters are illustrated in Figure 14.

Cluster 1 and 2 (red and green) have similar rheological parameters (Figure 14 a, e, f and g) but belong to different asphaltenes class (Figure 14 c). It appears that from a rheological point of view, the samples belong to

similar ageing states but not based on their asphaltenes, while it is known that asphaltenes increase during ageing. An assumption could be that the starting point of asphaltenes was different, but their evolution might have been similar. This assumption can lead us to the conclusion that those clusters might belong to a different supplier and/or different crude oil since SARA fractions strongly relate to the binder source. Therefore, PC2 may exhibit differences in the asphalt binder source. Cluster 3 shows the highest PC1 values and as it can be seen by the mean values of Figure 14, the highest values in Resin, R, $T_{c,m}$, $I_{C=O}$, which indicates the most aged samples. On the contrary, Cluster 4 shows the lowest PC1 value, thus the less aged group of binders with the highest ω_c and the lowest $I_{C=O}$. Consequently, it is evident that PC1 can illustrate the ageing state.

The results of the clustering analysis demonstrate also the inability of conventional properties (penetration, softening point and penetration index) to distinguish between the ageing state of RA binders and as a consequence to comprehensively characterise the RA binder.

Figure 15 shows the mean values of the three commonly used conventional properties among the defined clusters. Clusters 1 and 5 are in accordance with the high and low penetration groups. On the contrary, the intermediate penetration groups show no differentiation while the ageing state clusters do. The same observations apply also for softening point and the penetration index. The main reason behind this trend is that the conventional properties are able to roughly express the mechanical response of the material at intermediate and high temperature as the DSR does, but the ageing states are also based on chemical parameters ($I_{C=O}$ and part of SARA parameters), data that cannot be reflected by the conventional properties.

The result of the clustering analysis, based on PCA and HCA techniques, proved to be a very useful tool. As clearly illustrated, it offers the ability to explore and then define RA binder clusters based upon chemical and rheological properties that alter with ageing. Additionally, the clustering method can be further implemented as part of a decision-making tool. Such a tool can be used for various purposes. First, it could verify the suitability of certain RA materials for specific RA percentage range, for example lower or higher percentage depending on the ageing state cluster; second, it could verify the use of RA for certain pavement layers, for example less aged RA clusters could be used as part of surface asphalt layers, moderately aged clusters in base asphalt layers and highly in unbound base layer; lastly it could depict the need or not of certain additives, such as the use of rejuvenators for the more aged clusters.

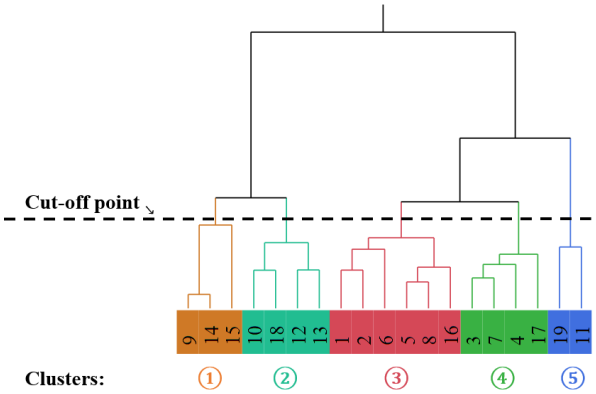


Figure 12: Dendrogram of HCA on the RA binders, based on selected variables; the cut-off point discriminates the five clusters.

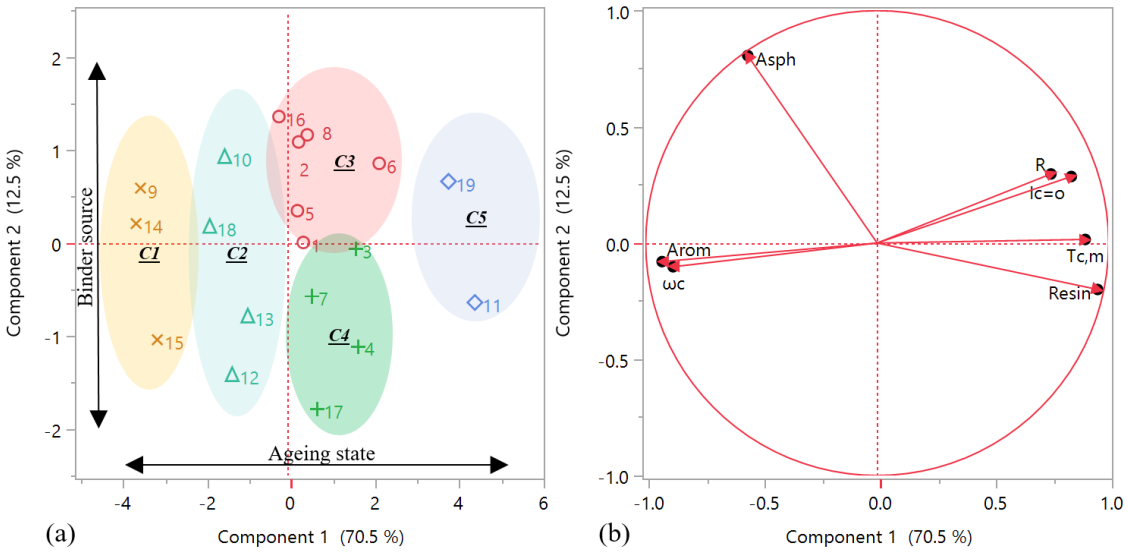


Figure 13: PCA score plot of the RA samples (a) and loading plot of the parameters based on PC1 and PC2 (b)

Table 2: Loading matrix of PC1 and PC2

Variable	PC1	PC2
Resin	**0.953**	-0.200
$T_{c,m}$	**0.899**	0.015
$I_{C=O}$	**0.839**	0.286
R	**0.751**	0.297
Asphaltenes	-0.559	**0.806**
ω_c	**-0.881**	-0.102
Aromatics	**-0.929**	-0.080

In bold loading factors >0.60

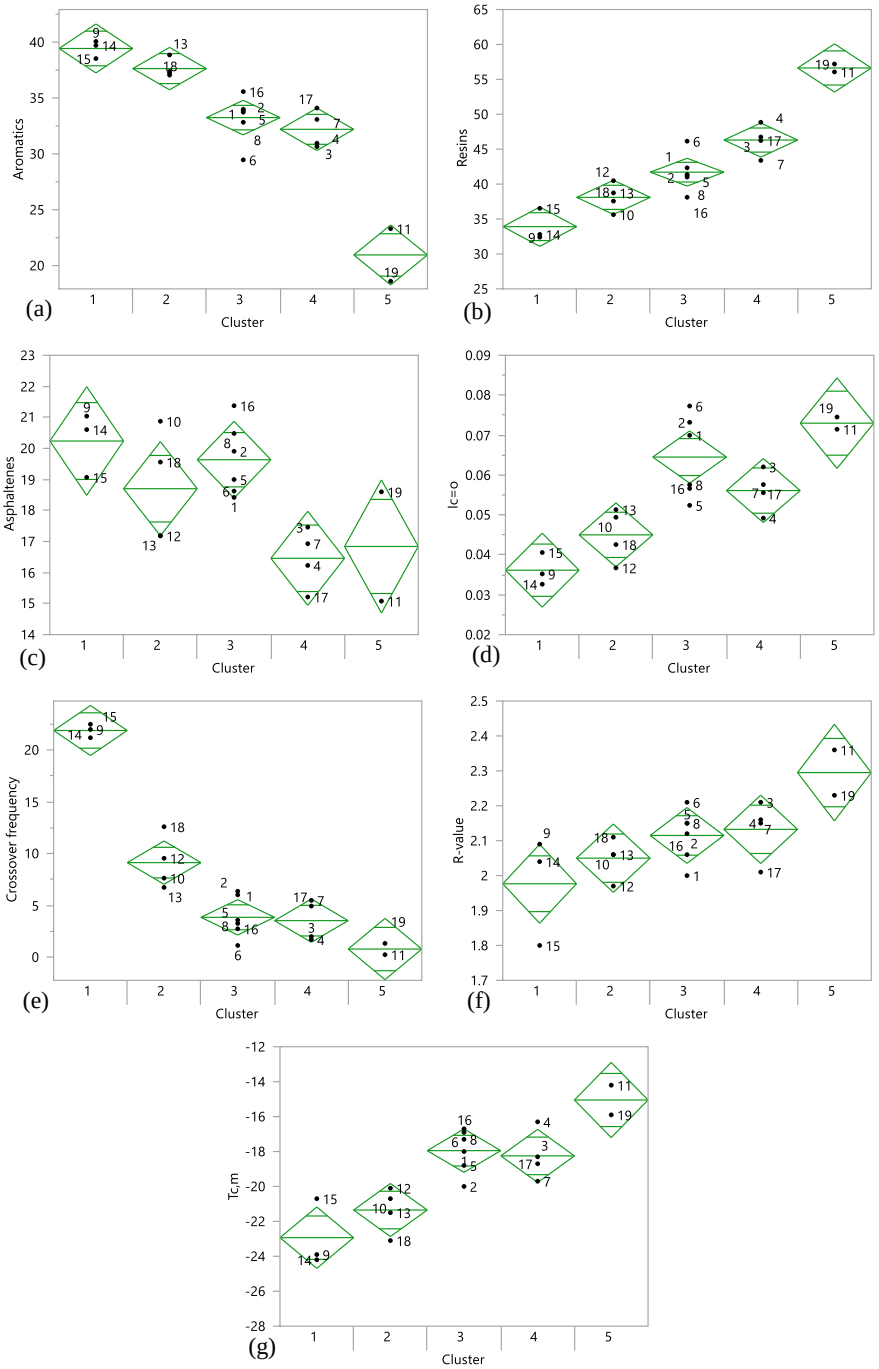


Figure 14: Mean value plots of the parameters inserted in the analyses against the defined clusters, a) aromatics, b) resins, c) asphaltenes, d) $I_{C=O}$, e) ω_C, f) R and g) ΔT_C.

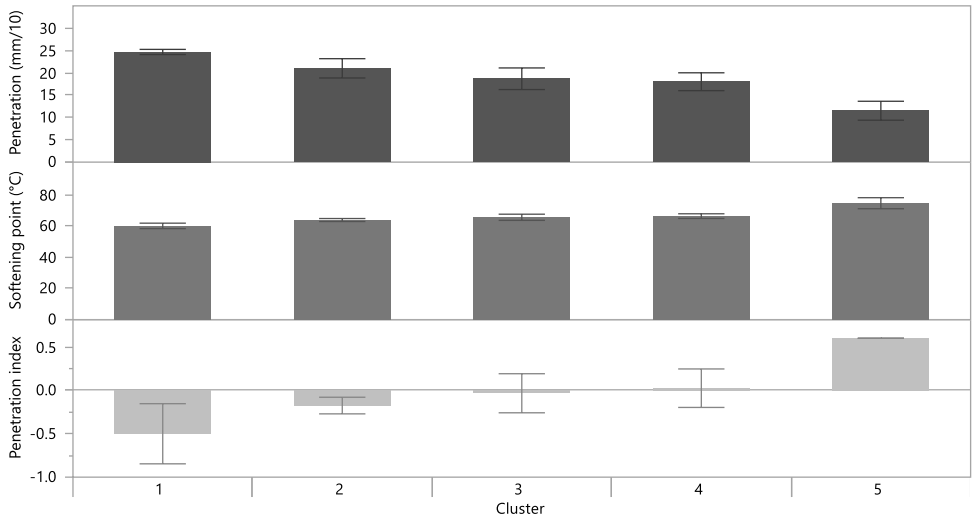


Figure 15: Mean values of conventional parameters (penetration, softening point and penetration index) for the defined clusters.

4. Conclusions

In this study, a set of different RA binders was evaluated, chemically and rheologically, and then statistically analysed using HCA and PCA techniques to detect patterns among them based on properties' similarities. Based on the experimental evaluation of 19 randomly collected RA binders, the following conclusions can be drawn:

- Rheological parameters showed differences in ageing of the RA binders, as also demonstrated in other studies. More aged asphalt binders showed a simultaneous increase of R and a decrease of ω_c.
- RA binders found to contain SBS traces exhibited almost similar or lower elasticity at higher temperatures, when tested using DSR, compared to non-modified RA binders.
- ΔT_c and $I_{C=O}$ did not demonstrate the same trend as the rheological properties, especially in the intermediate penetration group binders (15-20 mm/10). A possible explanation could be related to differences in the virgin binders, or to the different aging conditions the virgin materials were exposed to, and also to variations in the layer depth or the layer type they originate from.
- Conventional properties, such as penetration, softening point and penetration index, are less accurate compared to using a combination of chemical and rheological parameters to characterise the RA binders. Furthermore, conventional properties fail to demonstrate properties associated with distress phenomena such as G-R and ΔT_c, derived by DSR tests. Those properties are particularly important when it comes to ageing assessment.

Based on the HCA and PCA analyses:

- It has been demonstrated that pattern detection techniques (in this case HCA and PCA) can be utilised to detect clusters of asphalt binders with similar properties, reflecting this way the ageing state of each cluster.
- The variables inserted in the analyses, are reliable indicators that individually can provide insight about the ageing severity. The advantage of incorporating them in the HCA and PCA analyses is the demonstration of a combined chemo-rheological effect on the ageing states.
- Binders with the same penetration can belong to different clusters, indicating different ageing states.

- Clusters might also exhibit the source of the binder. This statement could have been more in-depth explored if more information concerning the element composition were analysed, such as nickel and vanadium content, but it was not in the scope of this research.
- The generic SARA fractions provided information concerning ageing but also information that can be attributed to the binder source, as illustrated by the PCA.

This study highlights the necessity of considering more advanced parameters (compared to the current conventional properties) and pattern detection techniques, for the comprehensive characterisation of the ageing state of RA materials. This approach is especially important for the optimisation of new mixtures with high recycling rates. The presented method is capable of distinguishing ageing states that can be further exploited to make decisions concerning the selection of RA materials for certain applications (e.g. certain pavement layers), to decide recycling rate thresholds or for the selection of additives (e.g. use of rejuvenators).

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Disclosure statement

No potential conflict of interest was reported by the authors.

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