Fundamental Investigation of the Interaction Mechanism between New and Aged Binders in Binder Blends

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ABSTRACT

Determining the permissible amount of reclaimed asphalt pavement (RAP) that can be incorporated in new pavement mixes is a design challenge for practitioners around the world. A major challenge in accomplishing this is the limited understanding regarding the interaction between the aged and unaged binders in these mixtures, and the ensuing physio-chemical phenomena. In this study, the solubility related molecular interactions of blended binders comprising of aged-unaged fractions was evaluated using an extension of the Hansen Solubility Parameter (HSP) model of solubility. Virgin binder was blended with aged binders from two different sources, at proportions of 15%, 30%, and 50% to prepare various blends. These blends were evaluated using a method of titrations, to identify their internal stability and relative extents of intermolecular interactions in terms of dispersive forces, hydrogen bonding, and polar interactions. The results implied that small proportions of aged binders have limited effect on the original stability of the unaged binders and may be incorporated into mixes without changes in mixture design. Further tests using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) revealed that the oxidative elements in the blended binders increased with the use of higher percentages of aged binders. It is theorized that these fractions will affect the polydispersity of the molecules through increased molecular associations. Overall, it is advised that incorporation of higher RAP contents in mixtures should ideally involve some consideration of the chemistries of the intermixing binders, in order to design the most compatible and appropriate blend.

Key words: RAP mixing, Compatibility, Oxidation, RAP binder, Bitumen ageing

1. Introduction

With the established environmental and monetary benefits, the use of reclaimed asphalt pavement (RAP) in new pavement construction has turned into a routine practice in many parts of the world (McDaniel *et al.* 2000). Although technical specifications in many countries allow for high RAP content, up to 50% or even more in new asphalt mixes, the average RAP content used in mixes generally does not exceed 20% under normal hot mix conditions (Al-Qadi *et al.* 2007). The usage of a higher percentage of RAP requires dedicated processing conditions and the use of additional softening agents. Such specialised techniques have only been refined and used in a few countries like Japan (West and Copeland 2015). One of the most significant limitations that prevent the extensive use of higher percentages of RAP is the lack of information concerning the variables involved in the blending of aged binder in RAP with virgin binder during the mixing process. Although many studies have been conducted regarding these issues, no conclusive and commonly applicable results have been found (Sreeram and Leng 2019). Specifically, a fundamental understanding regarding the interaction between new and aged binders is deficient, which leads to difficulties in predicting the performance and thermodynamic stability of the binder blends (Sreeram and Leng 2019).

The mixing of aged and unaged bitumen is an intricate process and involves the molecular interaction of various bitumen fractions that come together to form new associations. Aged bitumens are also markedly oxidised as a result of the natural ageing process of binders, which not only increases the stiffness but also causes significant changes in its chemical composition (Wu *et al.* 2010). These changes increase the relative extent of polar fractions in these binders, leading to the likelihood of amplified associations among its molecules (Jones and Kennedy 1991). It is reasonable to expect that blends of virgin and aged binders may exhibit different extents of intermolecular interactions in contrast to the original sources as a consequence of the various new molecular associations formed during mixing, and subsequent homogenisation. Therefore, the features involved in mixing these fundamentally different binders to create a blend with target properties is a critical aspect that needs to be explored and verified using different methods (Sreeram and Leng 2019). In fact, such a fundamental understanding is also vital to engineer recycling agents, modifiers and other alternative materials that can be utilised as binder extenders.

A possible method to study the interaction of aged and virgin binders is based on solubility and compatibility. Previous works have demonstrated that bitumen can be modelled as a dispersed fluid based on the mutual solubility of its continuum of molecules of varying polarities (Redelius 2000). The extent of such solubilities can be quantified using parameters that evaluate the interaction among its molecules in condensed states (Hildebrand 1936, Barton 2017). In the case of bitumen which consists of an innumerable number of molecules, parameters to evaluate its solubility would need to take the different types of interactions among them into consideration. The first studies regarding bitumen solubility made use of one-parameter models such as the Hildebrand parameter, which showed the change in internal energy of the condensed material and that of an ideal gas of the same material at the same temperature (Hansen 1967, Laux *et al.* 1997). This was further developed to use a more useful three-parameter model known as the Hansen Solubility Parameters (HSP) which took into consideration different molecular interactions, including dispersion interaction (δD MPa $^{1/2}$), dipole interaction (δP MPa $^{1/2}$) and hydrogen-bonding interaction (δH MPa $^{1/2}$), all of which are significant in the case of bitumen (Hansen 1967, Redelius 2000). Using this, the relative solubility between two materials can be estimated based on the “distance” between points in a three-dimensional coordinate system corresponding to HSP in three-dimensional space, referred to as “Hansen Space” (Hansen 1967). However, the method involved in determining HSP is unsuitable for routine measurements in bitumen. A more applicable approach to identify the solubility tendencies of different bitumens is based on a derivative of the HSP model and termed as the “bitumen solubility model” (BISOM) (Redelius 2000). Through BISOM, the relative extent of intermolecular interactions in the form of dispersive forces, hydrogen bonding, and polar interactions can be estimated using a method of turbidimetric titrations. Specifically, turbidimetric titrations can be carried out for bitumen using titrants that have different orientations in Hansen space, with each providing information regarding the internal stability and solubility related properties with respect to different molecular interactions in the Hansen model (Heithaus 1962, Redelius 2004).

In a previous work that analysed binders of varying ageing levels using a modified BISOM titration method, it was reported that aged binders and virgin binders could differ in terms of intermolecular interactions (Sreeram *et al.* 2019). It was also implied that the increased molecular agglomerations and low dispersibility of molecules in aged binders could affect its compatibility to be mixed with virgin binders, which in turn would dictate its mobilisation during mixing, subsequent blending, and long-term stability. Therefore, it is anticipated that the mixing of certain unaged-aged binder pairs could be more well-matched than others and the properties of the blend dependent on the individual chemistries of the various binders in the final mix. Nevertheless, there are only limited experimental and literature references regarding the compatibility of blended aged-unaged bitumens (Karlsson and Isacsson 2003). The present work is concerned with the evaluation of the solubility related molecular interactions of blended binders with different proportions of aged binder incorporated in them, using a modified version of the BISOM titration method. The results of these are then verified using tests such as Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and rheological analysis using a dynamic shear rheometer (DSR), to indicate the distinctive chemical and rheological characteristics of the blended binders. Overall, this work is guided with the expectation that it will allow researchers to comprehend the fundamentals involved in the chemistry and interaction mechanism of aged-virgin binder pairs. Such academic views are also projected to help facilitate in the improvement of current specifications in relation to RAP mixture design, including indicating the permissible amount of aged binder incorporation in HMA mixes.

2. Materials

Two differently aged binders were used to prepare the various blends in this study. The binders were extracted from two sources of RAP according to the procedure specified in AASHTO T164 and named as RAP-1 and RAP-2, respectively. The RAP materials were obtained from the local highways department and reported to be unmodified and of a moderate to high ageing state. Preliminary rheological analyses indicated that the binder from RAP-1 was stiffer than RAP-2. The virgin binder used was a commonly used local binder of PG high-temperature grade of 64 and low-temperature grade of -22^{o}C. Artificially blended (AB) mixes of the binders were prepared by blending the virgin binder with three different proportions of RAP binder at 15%, 30% and 50% by weight to prepare two series of binders. The mixing was conducted at a temperature of 165^{o}C using a mechanical mixer for a duration of 1 hour and a shear rate of 4000 r/min. The blended binders were labelled as AB-15-1, AB-30-1 and AB-50-1 for the binders prepared using RAP-1 (Series 1) and AB-15-2, AB-30-2, and AB-50-2 for the binders prepared using RAP-2 (Series 2), respectively. All chemicals used in this study were of laboratory grade purchased from Thermo Fisher Scientific. Also, it is well recognized that the total blending of RAP and virgin binders is dependent on mixing time, temperature and duration of retention. However, the goal of this study was not to emulate field blending, rather to study the compatibility of blends.

3. Experimental methods and procedure

3.1 BISOM titration

The titration method used in this work was based on the principle of turbidimetric titration.. This theory states that if two liquids of varying solubility parameters (δ^i and δ^j) are mutually soluble then the combined solubility parameter (δ) of the whole mixture will be proportional to the concentration of each liquid, and can be described mathematically by the following equation:

$$\delta = \frac{(\phi^i\,\delta^i + \phi^j\delta^j)}{(\phi^i + \phi^j)} \qquad (1)$$

where ϕ is the volume fraction of each liquid i and j. Using this equation, the solubility related parameters of a material can be calculated experimentally wherein the material under investigation is titrated in a solution with a non-solvent until the onset of precipitation. For bitumen, 0.75 gms of the sample was dissolved in 2 ml, 3 ml and 4 ml solutions of toluene in a closed flask to prepare three solutions of varying concentrations as per the procedure described in previous studies (Sreeram *et al*. 2019). These solutions were titrated with 1 ml aliquots of a non-solvent until the onset of precipitation. Based on the prior work conducted, three different non-solvents were selected with each representing different interactions in the Hansen solubility model, i.e. iso-octane, 2-butanone and 2-ethyl-1-hexanol; illustrative of the dispersive forces, hydrogen bonding interactions and polar interactions respectively. The solubility parameters for toluene, the non-solvents and bitumen (avg) are shown in Table 1. Figure 1 shows the plot of the HSP points of the solvents along with the HSP sphere of bitumen, which entails its entire solubility in Hansen space. The solubility sphere of bitumen was calculated as per the following equation:

$$R_a{}^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \qquad (2)$$

where:

R_a=distance between a solvent and bitumen,

δ_{d1} (or δ_{p1} or δ_{h1}) = dispersion component of the solvent,

δ_{d2} (or δ_{p2} or δ_{h2}) = dispersion component of bitumen

The procedure followed involved using a version of the filter paper method, conducted in a previous work (Sreeram *et al.* 2019). Following this, after the addition of each 1ml aliquot of titrant, a small drop was removed from the titration solution and placed on a filter paper. This was continued until the formation of two distinct rings, which is indicative of the commencement of flocculation (Heithaus 1962). The total volume of titrant added at the flocculation point was noted. Two parameters were calculated for each titration, i.e., flocculation ratio (FR) and concentration (C), using the following equations:

$$FR = \frac{V_S}{V_S+V_T} \quad (3)$$

$$C = \frac{W_A}{V_S+V_T} \quad (4)$$

where V_s is the volume of solvent, V_T is the volume of titrant and W_A is the mass of bitumen. The values for FR and C at each concentration were plotted on a graph. The intercepts on the corresponding x and y axes were obtained through the linear regression of the points and denoted as C_{min} and FR_{max} respectively. Using these intercepts, further calculations were performed to obtain the various solubility-based parameters for the tested binders. The dispersive interactions with iso-octane were denoted with the letter D, polar forces with 2-butanone was termed with the letter N, and hydrogen bonding interactions with 2-ethyl-hexanol was denoted with the letter H. The parameter D_a (or N_a or H_a) was calculated as follows:

$$D_a = 1 - FR_{max} \quad (5)$$

The subsequent parameter D_0 (N_0 or H_0) was calculated by:

$$D_0 = FR_{max}\ [\left(\frac{1}{C_{min}}\right) + 1] \quad (6)$$

Finally, using D_a and D_o, parameter D (or N or H) was calculated as shown below:

$$D = \frac{D_0}{1-D_a} \quad (7)$$

This parameter D (or N or H) is a measure of the stability of the binder in relation to the various molecular interactions in the HSP model. It also serves as an indicator of the relative strength of the three different interactions in it.

3.2 Fourier-transform infrared (FTIR) spectroscopy

The FTIR tests were conducted on the samples to identify the differences in oxidation exhibited between them. The ageing of bitumen is a widely researched topic and the natural oxidation of asphalt binders over time is an established concept in bitumen chemistry (Ding *et al.* 2016).

The carbonyl band (C=O) around 1700 cm^{-1} and the sulphoxide band (S=O) at around 1032 cm^{-1} exhibited by binders are the major functional groups used to gage the level of oxidation among binders. However, the carbonyl band has been more frequently used to relate to the level of long-term ageing (Bowers *et al.* 2014a). Numerous studies have shown that aged binders exhibit significantly higher levels of C=O bonds as compared to unaged binders, which exhibit insignificant or zero intensity of C=O bond at this wavelength (Sreeram *et al.* 2018, Sreeram and Leng 2019). These differences in oxidation between binders have been used to correlate various aspects of binder rheology and chemistry (Sreeram *et al.* 2018). In this study, the extent of oxidation exhibited by the binders was quantified using a previously reported method (Hofko *et al.* 2017). The analysis approach adopted for all the FTIR spectra involved the integration of areas, normalised spectra, and absolute baseline. Mathematically, the area of analysis of a single spectrum was calculated using the following equation:

$$\text{IA}=\int_{w_{l,oa}}^{w_{u,oa}} VA_{norm}(w)\, dw \qquad (8)$$

where IA is the normalised integrated area; $w_{u,oa}$ is the upper wavenumber limit for the structural group; $w_{l,oa}$ is the lower wavenumber limit for the structural group and $VA_{norm}(w)$ is the normalised absorbance at wavenumber w. The carbonyl band was specified from 1666 to 1746 cm^{-1} (Hofko *et al.* 2017). Figure 2 shows the FTIR spectrum of a sample virgin binder and RAP binder, which demonstrates the increased oxidation peak at the wavelength of around 1,700 cm^{-1} for the RAP binder. The figure also illustrates the analysed area of interest in the FTIR spectra. The analysis was conducted using a Bruker Vertex 70 Hyperion 1000 spectrometer with a diamond ATR module. A resolution of 4 cm^{-1} was used to record the spectra from 4000 to 400 cm^{-1} in a reflective mode. For this test and the GPC test described below, the tests were performed in duplicates as repeatability is an inherent concern when considering the characterization of bitumen with such tools. All chemical and rheological test results in this study present an average result of the two tests performed.

3.3 Gel permeation chromatography (GPC)

GPC, widely referred to as size exclusion chromatography was used to separate molecules of bitumen into various sizes and characterise its complete weight distribution. GPC analysis has been extensively utilised in bitumen research in the past and found to be suitable to study the aging-related behaviour of binders (Bowers *et al.* 2014b). A Shimadzu Prominence GPC system using two styragel columns was used to test the samples. The dissolution of the binders to the required concentration was conducted using tetrahydrofuran (THF), followed by the subsequent filtration through a 0.2 µm filter. Figure 3 shows the illustrative chromatogram of a sample virgin binder and RAP binder. The large molecular size (LMS) percentages of the samples were calculated from each GPC chromatogram as follows (Kim *et al.* 2006):

$$\text{LMS\%} = \frac{\text{Area of first}\,\frac{5}{13}\,of\ chromatogram}{\text{Toal Area below the chromatogram}} * 100 \qquad (9)$$

3.4 Dynamic shear rheometer (DSR)

DSR was used to gage the rheological characteristics of the original binders and binder blends. For binders containing recycled materials, the intermediate and low-temperature properties are of particular concern, due to the increased likelihood of cracking in these stiff materials. In most cases, the bending beam rheometer (BBR) is utilised for low-temperature characterization of binders. However, for materials where only small quantities are available for testing, such as is usually the case for extracted RAP binders, the DSR in combination with the 4 mm plate geometry has been shown to be a suitable surrogate for BBR testing (Sui *et al.* 2011). In this study, DSR tests were conducted using a TA Instruments rheometer that was calibrated for temperature and inertia effects as described in previous works (Hajj *et al.* 2019). Temperature-frequency sweeps were run at temperatures ranging from -18°C to 40°C and frequencies ranging from 0.1 Hz to 15 Hz. At low temperatures, normal force control was used to ensure adhesion between the plate and the specimen as conducted in the previous study (Hajj *et al.* 2019). The master curves for each were constructed at a reference temperature of 0°C using the time-temperature superposition principle. The master curve was created using a sigmoidal function as follows:

$$\log(|G^*|) = \delta + \frac{\alpha}{1+e^{\beta-\gamma\log(t_r)}} \qquad (10)$$

where $|G^*|$ = the dynamic modulus of the material, δ = the lower asymptote of the material modulus, t_r = reduced time, and α, β, and γ = shape factors for the function. Reduced time is calculated based on multiplying the test time (in the frequency domain) with a shift factor that converts it to an equivalent time at the reference temperature, in this case, 0°C. Shift factors were generated using the Williams-Landel-Ferry (WLF) equation, although when shifting data to the master curve, the discrete shift factors obtained from the DSR test were used. It is recognised that a lower asymptote in a sigmoidal shape is not applicable for binders without particulate matter. However, the choice of this model was based on previous studies that indicated a better fit by this model in the region of interest (Hajj et al. 2019).

4. Results and discussion

4.1 Solubility based molecular interactions

The parameters related to the various molecular interactions in the Hansen model was calculated as per the titration procedure described earlier. The results corresponding to the relative molecular interactions, i.e., dispersive forces (D), polar interactions (N) and hydrogen bonding (H) interactions are presented in Figure 4. It was seen that both RAP binders in Series 1 and Series 2 displayed different extent of interactions in comparison to the virgin binder. Similar findings were reported in a previous study and ascribed the differences in interactions as a result of the increased molecular associations and agglomeration (Robertson *et al.* 1991, Sreeram *et al.* 2019). The differences in interactions such as polar interactions (N) is also associated with the higher content of the more polar fractions in aged bitumen, such as asphaltenes (Sreeram *et al.* 2019). As a result, the increased associations among molecules are known to lower its dispersibility thereby physically hardening bitumen. This stiffening of binders has a significant effect in terms of rheology and can potentially lead to the detrimental performance of aged binders in terms of long-term fatigue and thermal cracking performance (Al-Qadi *et al.* 2007, Sreeram *et al.* 2018).

When comparing the artificially blended (AB) binders, the results varied. In general, the AB binders showed different D, H, and N values in contrast to the virgin binder and RAP binders. This was expected as AB binders are a combination of its constituents and will naturally have different chemical compositions in comparison. The AB binders are expected to exhibit the relative extent of molecular interactions in proportion to the various new associations formed after mixing, subsequently reaching a state of molecular homogeneity. As per the molecular model of bitumen described by Gray et al. *(2011),* intermolecular interactions in binders include molecular recognition and host-guest interaction in three-dimensional porous networks. In virgin-aged binder blends, new associations would likely be formed among molecules during mixing, depending on the individual compositions of the binders leading to changes in the extent of intermolecular forces. Further, it was interesting to note that in both sets of binders i.e. Series 1 and Series 2, the binders incorporated with 15% RAP showed results similar to those of the virgin binder. It can be inferred that the inclusion of the aged binder at lower proportions has a limited effect on the internal stability of the virgin binder. In terms of the dispersed fluid model of bitumen, it signifies that the virgin binder has enough solvable components to fully solvate the added aged binder and retains similar solubility tendencies. However, when 30% and 50% RAP are added, there is more variation in results. In both cases, AB-30 and AB-50 binders exhibited lesser values for D as compared to the virgin binder which may indicate that the internal stability of those binders are different than the virgin binder. It must be noted that these changes in internal stability cannot specify that any binder is superior to another in terms of rheology but can only indicate a relative difference, which will evidently have performance based consequences. Previous studies have however indicated that binder exhibiting very low values for D, such as the aged binders in this study, may exhibit low peptizability and could be thermodynamically unstable (Redelius 2000). In addition, the binder AB-50-2 also showed an increase in the N parameter as compared to AB-50-1. This can be credited to the specific composition of the RAP binders, and its effect will become more significant as the RAP content increases. Overall, the results suggest that small concentrations of RAP will not lead to a significant change in the internal stability of the binders. Although these results indicate that there are changes in internal stabilities in binder blends, it is difficult to comprehend the effects of these interactions in terms of well estabished bitumen microstcruture models . Further chemical and rheological analyses are required to identify the possible mechanisms of interaction and are discussed further.

4.2 Extent of oxidative groups

The areas corresponding to the carbonyl bonds in the blends were calculated as per the procedure described in 3.2 and the results are indicated in Figure 5. Similar trends for oxidation were observed for both sets of binders. As expected, the areas under the carbonyl bonds exhibited by the RAP binders were significantly higher than that exhibited by the unaged virgin binders, as a result of the natural oxidation over time. The pathways of this oxidation have been explained by many studies in the past, indicating the transformations of aliphatic sulphides to sulphoxides and benzyclic carbon to carbonyl groups (Petersen 2009). During oxidation, the molecular structures of binders are altered through the dissociation, isomerization, and fragmentation of the asphaltene molecules, the dissociation of aromatics molecules, and the association, cyclization, and dissociation of saturate molecules. This is reflected in the possible reaction types occurring during oxidation, introduced in the study by Siddiqui (1991) and represented in Figure 6 (Siddiqui and Ali 1999). These oxidized components and other oxygen-containing by-products formed during ageing are polar species that interact with other polar species, increasing the overall polarity of the binders.

The incorporation of the RAP binders was seen to increase the overall oxidative products in the AB binders, and this trend increased continuously with the percentage of RAP added. Although these FTIR results cannot be considered to be rigorously quantitative, it can be used to semi-quantitatively confirm that the extent of oxidative species is higher in the AB binders. Additionally, no chemical reaction is assumed to occur between RAP binders and virgin binders, hence the relationship is expected to be fairly linear (Sreeram *et al.* 2018). More polar, oxygen-containing functionalities are expected to exist in the RAP binders which propagate the agglomeration of certain fractions such as asphaltenes (Petersen 2009, Le Guern *et al.* 2010). When a small proportion of RAP binder is blended with the unaged binder, the total oxidative products in the combined binder are slightly increased. However, from the solubility results, it can be observed that the internal stability of the binders stayed relatively similar. On the other hand, at higher concentrations of RAP binder, the internal stability of the combined binder changes, resulting in the variation of the solubility properties. In a well dispersed and stable bitumen, the solvency of the more polar species is matched by the dispersing power of the solvent species. A change in this power causes a change in the overall solubility and internal stability of the bitumen. However, this would be related to the individual chemical composition of the binders and cannot be generalized as such. Previous studies have also shown oxidized asphaltene fractions would have an affinity towards non-oxidized fractions and interact through various π- π interactions (Choi *et al.* 2017). The extent of this interaction will naturally depend on the concentration of the aged fractions in the mixture and will hence vary with concentration as discussed in the next section.

4.3 GPC parameters

The LMS fractions of the binders were calculated as per the procedure described in Section 3, with the results presented in Figure 7. Studies have shown that fractions containing higher extents of oxidation products are mainly represented in the LMS fraction of the GPC chromatogram (Sreeram *et al.* 2018). This is mainly attributed to the association of smaller molecules with higher polarities during aging, which then contribute to the LMS fraction (Dukatz *et al.* 1984, Hattingh 1984). Firstly, it is important to understand the premise of molecular size distribution in bitumen. Bitumen entails a band of fairly large hydrocarbons with dissimilar sizes, polarity, and aromaticity, with the smallest size of hydrocarbons defined by the respective processing conditions of the crude oils (Redelius and Soenen 2015). A good correlation could be noticed with the FTIR results, as in the binders exhibiting the highest levels of oxidation also showed higher percentages of LMS. The LMS % calculated ranged from 13.8 % for the virgin binder to 21.6% and 19.6% for RAP-1 and RAP-2 respectively. The AB binder ranged in between these values and the levels of LMS were seen to increase with the increase in RAP percentage, thereby validating that the levels of oxidative species are also higher in those binders.

The mechanism of introducing more oxidized species present in RAP binders into unaged binders can be explained in terms of the polydispersity of its molecules. Polydispersity in this case referring to the random and non-uniform distribution of molecules in the binder. The overall increase in polarity in the aged binders promotes the tendency of its polar fractions, such as asphaltene molecules to agglomerate and form nanoaggregates as illustrated in Figure 8 (a) (Mullins 2010, Zadshir *et al.* 2019). When these species are introduced in unoxidized binders during mixing, some changes in the polydispersity of molecules can be expected. These oxidized asphaltene molecules will have a potent affinity towards non-oxidized asphaltenes via π-π stacking, hydrogen bonding, and acid-base interactions. The addition of such oxidized fractions would facilitate the further agglomeration of molecules, the formation of larger aggregates and reduction of its overall polydispersity (Choi *et al.* 2017). This is represented in the schematic diagram of the interaction mechanism as shown in Figure 8 (b). However, the extent of this agglomeration will depend on the concentration of oxidized species in the blend and overall peptizability of the maltene phase. Hence, when RAP binder is added at small concentrations, there is not much change in the stability and extent of interactions in the combined blend. Moreover, not all molecular fractions in the aged binders are oxidized and such binders will also possess unreacted elements.

4.4 Rheological results

The rheological parameters of the two sets of binders were measured as described in Section 3.4, and the respective master curves are shown in Figure 9a and Figure 9b respectively. At the higher temperatures (from 10°C to 40°C) tested in this study, a distinct difference was seen between the stiffness of the binders with different contents of RAP. The virgin binder alone was the softest binder whereas both RAP binders exhibited the stiffest behaviour. The stiffness of the AB binders increased in proportion to the concentration of RAP binder in it, for both series. The difference in material behavior becomes more evident at elevated temperatures and low frequencies but is observable throughout a large portion of the master curve. At high temperatures, on average, the calculated G* for both RAP binders were seen to be around 10 times greater than the virgin binder, while for AB-15 this difference was around 0.5 times and it increased to approximately 3 times for AB-50. One mechanism for the rise in stiffness with the increase in RAP content is through the increase in particle attraction (Petersen 2009). The increased polar molecules in the aged binders tend to associate with each other to form organized structures through the solvent phase of the non-polar material. Such attraction between molecules can lead to the formation of three-dimensional structures leading to the hardening of bitumen. The strength of this organization of the structures would naturally depend on the extent of dispersive power of the continuous phase. An increase in the quantities of aged binders leads to higher levels of organizations, thereby stiffening the material and increasing its ability to resist external forces (Petersen 2009). Such an increase in modulus can be predicted by Einstein's theory of colloids and further modifications based on the Pal-Rhodes model (Einstein 1906, Pal and Rhodes 1989).

4.5 Recommendations for mixture design

Aged binders and unaged binders are fundamentally dissimilar in terms of chemistry and understanding the full extent of the features involved in their blending is challenging. In view of this, there are many intricacies for practitioners to consider in order to achieve a reasonable blend with target properties. Most agency specifications currently indicate that at RAP percentages of 15% or less, no change in virgin binder grade is required (Al-Qadi *et al.* 2007). It is important to bear in mind that these specifications were mainly designed based on rheology and to achieve desired mechanical properties, without the consideration of binder chemistry and long-term integrity of the blends. As seen from the results of this study, binders blended at those ratios exhibit similar trends of molecular interactions as the unaged binder that serves as its main constituent. Therefore, it is possible that low contents of RAP may be incorporated into mixtures without much deliberation or change in mixture design, irrespective of RAP source. This could be important in terms of practice as screening, sorting and stockpiling of RAP sources is a big challenge, especially in countries where land space is premium. At higher RAP percentages, mixture design becomes more complicated. Introducing more fractions of aged components would noticeably affect the intermolecular forces in the blended binders and possibly its long-term stability. Dependent on the strength of these interactions, its introduction may exhibit a governing influence on the overall molecular interactions leading to variability in properties of the blend (Sreeram *et al.* 2019). In a blend with higher percentages of RAP, the overall solvency power of the solvent phase must be sufficient to fully disperse the asphaltenes and achieve relative homogeneity. Softening the blended binders by lowering the grade of the virgin binders may allow reaching the target rheological properties, however, this does not necessarily reflect the internal stability in the blend. Some consideration of the chemistries is essential as even though binders may exhibit similar rheological characteristics, they may be different in chemical compositions (Petersen 2000). These differences could lead to performance issues for the binder that are not accounted for by the rheological parameters. Currently, there are no standards or frameworks for evaluating the compatibility between binders and further research is recommended.

5. Findings and conclusion

In this study, the differences in solubility related molecular interactions were examined for unaged binders modified with different concentrations of RAP binders from two sources, using an extension of the Hansen model of solubility, and other chemical and rheological tools. The following findings were drawn from laboratory tests:

- Binders modified with low percentages (~15%) of RAP binders showed similar extents of internal stabilities as compared to the unaged binder.
- Increased concentrations of RAP binders altered the extent of internal stability in the combined blends and are consequently expected to have implications in terms of binder compatibilities and blend homogeneity. However, based on the source or concentration of RAP binder, it does not appear that the mechanism of the interaction significantly changes, rather, it is just magnified by a higher ratio of RAP binder.
- The oxidative elements in the combined binders were seen to increase with the increase in percentages of RAP binders. It is postulated that these fractions will affect the polydispersity of the molecules through increased molecular agglomerations and associations. In terms of rheology, an increase in stiffness was observed on the addition of higher concentrations of aged binder.
- Overall, it was detected from the chemical and rheological analyses that there was a continuous change in the observed parameters of each test with the increase of RAP binder in the blends, without the presence of any discontinuities.

- Low content of RAP may be incorporated into mixtures without any change in the mix design. However, using higher RAP content (more than 15%) in mixes may require some consideration of the chemistries of the intermixing binders, in order to design the most appropriate blend.
- A limitation of this study was that the titration procedure adopted can only indicate the relative differences in solubility tendencies between samples and is not an exact measurement. Further, the artificial mixing considered in this study may not precisely be the same as what occurs in the field, where the full blending efficiency realised in a laboratory environment may not be achieved.

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References

Al-Qadi, I., Elseifi, M. & Carpenter, S., 2007. *Reclaimed asphalt pavement–a literature review. Illinois center of transportation*.

Barton, A.F., 2017. *CRC handbook of solubility parameters and other cohesion parameters*: Routledge.

Bowers, B.F., Huang, B., Shu, X. & Miller, B.C., 2014a. Investigation of reclaimed asphalt pavement blending efficiency through gpc and ftir. *Construction and Building Materials,* 50, 517-523.

Bowers, B.F., Moore, J., Huang, B. & Shu, X., 2014b. Blending efficiency of reclaimed asphalt pavement: An approach utilizing rheological properties and molecular weight distributions. *Fuel*, 135, 63-68.

Choi, S., Choi, S.Q., Kim, J.-D. & Nho, N.-S., 2017. Partially oxidized asphaltene as a bitumen viscosity reducer. *Energy & Fuels,* 31 (9), 9240-9246.

Ding, Y., Huang, B. & Shu, X., 2016. Characterizing blending efficiency of plant produced asphalt paving mixtures containing high rap. *Construction and Building Materials*, 126, 172-178.

Dukatz, E., Anderson, D. & Rosenberger, J., Year. Relationship between asphalt flow properties and asphalt composition (with discussion)ed.^eds. *Association of Asphalt Paving Technologists Proceedings*.

Einstein, A., 1906. Eine neue bestimmung der moleküldimensionen. *Annalen der Physik,* 324 (2), 289-306.

Gray, M.R., Tykwinski, R.R., Stryker, J.M. & Tan, X., 2011. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy & Fuels,* 25 (7), 3125-3134.

Hajj, R., Filonzi, A., Rahman, S. & Bhasin, A., 2019. Considerations for using the 4 mm Plate Geometry in the Dynamic Shear Rheometer for Low Temperature Evaluation of Asphalt Binders. *Transportation Research Record,* 2673 (11), 649-659.

Hansen, C.M., 1967. The three dimensional solubility parameter. *Danish Technical: Copenhagen*, 14.

Hattingh, M., Year. The fractionation of asphalted.^eds. *Association of Asphalt Paving Technologists Proceedings*.

Heithaus, J., 1962. Measurement and significance of asphaltene peptization. *J. Inst. Pet,* 48 (458), 45-53.

Hildebrand, J.H., 1936. Solubility of non-electrolytes.

Hofko, B., Alavi, M.Z., Grothe, H., Jones, D. & Harvey, J., 2017. Repeatability and sensitivity of ftir atr spectral analysis methods for bituminous binders. *Materials and Structures,* 50 (3), 187.

Jones Iv, D.R. & Kennedy, T.W., 1991. The asphalt model: Results of the shrp asphalt research program. *Transportation Research Board VTI Rapport A,* 372, 83-90.

Karlsson, R. & Isacsson, U., 2003. Bitumen structural stability characterization using turbidimetric titration. *Energy & fuels,* 17 (6), 1407-1415.

Kim, K.W., Kim, K., Doh, Y.S. & Amirkhanian, S.N., 2006. Estimation of rap's binder viscosity using gpc without binder recovery. *Journal of materials in civil engineering,* 18 (4), 561-567.

Laux, H., Rahimian, I. & Butz, T., 1997. Thermodynamics and mechanis of stabilization and precipitation of petroleum colloids. *Fuel processing technology,* 53 (1-2), 69-79.

Le Guern, M., Chailleux, E., Farcas, F., Dreessen, S. & Mabille, I., 2010. Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging. *Fuel,* 89 (11), 3330-3339.

Mcdaniel, R.S., Soleymani, H., Anderson, R.M., Turner, P. & Peterson, R., 2000. Recommended use of reclaimed asphalt pavement in the superpave mix design method. *NCHRP Web document,* 30.

Mullins, O.C., 2010. The modified yen model. *Energy & Fuels,* 24 (4), 2179-2207.

Pal, R. & Rhodes, E., 1989. Viscosity/concentration relationships for emulsions. *Journal of Rheology,* 33 (7), 1021-1045.

Petersen, J.C., 2000. Chemical composition of asphalt as related to asphalt durability. *Developments in petroleum science,* 40, 363-395.

Petersen, J.C., 2009. A review of the fundamentals of asphalt oxidation: Chemical, physicochemical, physical property, and durability relationships. *Transportation Research Circular,* (E-C140).

Redelius, P., 2000. Solubility parameters and bitumen. *Fuel,* 79 (1), 27-35.

Redelius, P., 2004. Bitumen solubility model using hansen solubility parameter. *Energy & fuels,* 18 (4), 1087-1092.

Redelius, P. & Soenen, H., 2015. Relation between bitumen chemistry and performance. *Fuel,* 140, 34-43.

Robertson, R.E., Branthaver, J., Plancher, H., Duvall, J., Ensley, E. & Harnsberger, P., 1991. *Chemical properties of asphalts and their relationship to pavement performance*.

Siddiqui, M.N. & Ali, M.F., 1999. Investigation of chemical transformations by nmr and gpc during the laboratory aging of arabian asphalt. *Fuel*, 78 (12), 1407-1416.

Sreeram, A. & Leng, Z., 2019. Variability of rap binder mobilisation in hot mix asphalt mixtures. *Construction and Building Materials*, 201, 502-509.

Sreeram, A., Leng, Z., Hajj, R. & Bhasin, A., 2019. Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended hsp model of solubility. *Fuel*, 254, 115578.

Sreeram, A., Leng, Z., Zhang, Y. & Padhan, R.K., 2018. Evaluation of rap binder mobilisation and blending efficiency in bituminous mixtures: An approach using atr-ftir and artificial aggregate. *Construction and Building Materials*, 179, 245-253.

Sui, C., Farrar, M.J., Harnsberger, P.M., Tuminello, W.H. & Turner, T.F., 2011. New low-temperature performance-grading method: Using 4-mm parallel plates on a dynamic shear rheometer. *Transportation research record*, 2207 (1), 43-48.

West, R. & Copeland, A., 2015. High RAP asphalt pavements: Japan practice - lessons learned. Lanham, MD: National Asphalt Pavement Association.

Wu, S., Pang, L., Liu, G. & Zhu, J., 2010. Laboratory study on ultraviolet radiation aging of bitumen. *Journal of Materials in Civil Engineering*, 22 (8), 767-772.

Zadshir, M., Hosseinnezhad, S. & Fini, E.H., 2019. Deagglomeration of oxidized asphaltenes as a measure of true rejuvenation for severely aged asphalt binder. *Construction and Building Materials*, 209, 416-424.