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CHARACTERIZATION OF COMPATIBILITY BETWEEN AGED AND UNAGED BINDERS IN BITUMINOUS MIXTURES THROUGH AN EXTENDED HSP MODEL OF SOLUBILITY

[1,2]Anand Sreeram, [1*] Zhen Leng, [2] Ramez Hajj, [2*]Amit Bhasin
[1] Department of Civil and Environmental Engineering
The Hong Kong Polytechnic University, Hong Kong SAR
[2] Department of Civil, Architectural and Environmental Engineering
The University of Texas at Austin, Austin, Texas, USA
*corresponding authors
Email: zhen.leng@polyu.edu.hk, a-bhasin@mail.utexas.edu

Abstract

Asphalt binders in bituminous mixtures with reclaimed asphalt pavement (RAP) comprise fractions of both aged and unaged binders, existing as a single entity. The degree of blending between the aged and virgin binder dictates the extent of homogeneity of the binder in the mix and consequently its mixture performance. However, their mechanism of interaction is still not well understood. In this study, a fundamental measure of compatibility between aged binders and unaged binders was evaluated exercising an extension of the Hansen Solubility Parameter (HSP) model of solubility. Nine binders consisting of unaged binder, field aged binders and artificially aged binders were tested using a method of turbidimetric titrations, to identify the internal stability of the binders and relative extents of different intermolecular interactions in terms of dispersive forces, hydrogen bonding and polar interactions. The results show that some aged and unaged binders noticeably differ in terms of polar interactions, which may lead to low dispersibility of molecules and increased molecular associations. These findings were further corroborated by chemical composition analysis based on saturates, aromatics, resins and asphaltene (SARA) fractionation which verified that the content of the highest polar fraction, i.e., asphaltene, was considerably higher in the aged binders. Overall, the study indicated that there are noteworthy differences in internal stability and composition between aged and unaged binders. Consequently, mixing of certain virgin-aged binder pairs could be more compatible than others based on their solubility parameters. To attain a homogenous blend while incorporating RAP, a more careful and detail-oriented approach that considers chemistries and inter-solubility of these components is recommended.

Keywords: RAP mixing, Compatibility, Polarity, RAP Binder, Bitumen Ageing

1. Introduction

Effective reuse of reclaimed asphalt pavement (RAP) has become an environmental and economic necessity in many parts of the world. An important design consideration for mixtures containing RAP is the influence of the recycled binder during the mixing process. Several current specifications regarding RAP mixture design assume that all the binder covering RAP aggregates is available to be blended with the virgin binder during mixing [1]. Further, it is implicit in this assumption that RAP binder completely homogenises with the virgin binder to generate a blend with target properties [2]. However, numerous studies conducted in this regard have reported variable results. It has also been reported that mixing conditions such as temperature, additives and material properties of the RAP binder affect the extent of this blending [3,4]. Nevertheless, very few studies have looked into the fundamental mechanism of interaction when virgin binder is added into RAP, and its effect on the RAP binder mobilisation and blending process.

During the mixing process, the virgin binder can be regarded as a solvent for the aged binder coating RAP, which dissolves and "rejuvenates" it, to the extent where some or all the RAP binder will become available to be blended with the virgin binder. It is therefore critical to understand and model the interaction between the RAP binder and virgin binder, as its scope will affect the amount of RAP binder available to be mixed. Although one can argue that high mixing temperatures and mechanical energy of mixing may ensure a reasonable blend between RAP binder and virgin binder, the question remains whether such forced blends of different binders can remain homogenous and stable over long periods of time.

A promising method to model this interaction between the RAP binders and virgin binders is based on mutual solubility and compatibility. Every bitumen is unique and contains millions of different molecules with varying polarities and two main schools of thought exist regarding the co-existence of these diverse molecules. One suggests that these molecules synchronize with each other in a dispersed state in the bitumen matrix, whereas the other suggests that these molecules tend to form associations based on their relative polarities, and the associated molecules exist in the form of a stable colloid [5,6] When considering the mixing of RAP binder and virgin binder in mixtures, if the RAP binder is completely soluble in the virgin binder, it can be inferred that the RAP binder is mobilised during mixing and the blended mixture is mutually compatible. However, if there is partial solubility and incompatibility between binders, it is problematic to assume full blending and mobilisation. Such scenarios introduce the possibility of producing underasphalted mixtures which can lead to long term implications in terms of performance, especially in relation to moisture damage and fatigue cracking [4]. To the best knowledge of the authors, there have only been limited studies that have examined the solubility and molecular interactions in bitumen with regard to aged binders, and its effect on recyclability [7]. In light of this, the aim of the current work is to evaluate this fundamental compatibility between virgin and RAP binders. It is expected that this study will allow researchers to better understand the mechanism and features involved in the blending of such binders, and facilitate the improvement in the current specifications in relation to mixture design and materials selection.

2. Background on Bitumen Compatibility and Solubility

The most commonly used models describe bitumen as a colloidal dispersion of asphaltene micelles in an oil-like medium of maltenes. However, other researchers have hypothesized that bitumen can be modelled as a dispersed fluid based on the mutual solubility within its various polar fractions [5]. The solvency of materials can be quantified through its solubility parameters, which are based on the evaluation of the interaction between its molecules in condensed states [8,9]. As bitumen consists of a complex mixture of millions of different molecules with varying degrees and types of interactions between them, parameters to evaluate the mutual solubility between bitumens or between a bitumen and an extended agent such as an extender or rejuvenating oil would need to take these interactions into consideration. The earliest works related to bitumen and crude oil solubility used the Hildebrand parameter, which expressed the difference in internal energy of the condensed material and that of an ideal gas of the same material at the same temperature [10,11]. It was mathematically defined as:

$$\partial = \sqrt{\frac{\Delta H_V - RT}{V_m}}$$

Where:
$\Delta H_V - RT$ = Heat of vaporization
V_m = Molar volume in the condensed phase.

However, one limitation of this parameter is that it does not take into account different forces between molecules such as hydrogen bonding and polar interactions, both critical in the case of bitumen. To overcome this restriction, other studies have used a three-parameter model known as the Hansen Solubility Parameters (HSP) which takes into consideration different interactions between molecules such as dispersion interaction (δ_D MPa $^{1/2}$), dipole interaction (δ_P MPa $^{1/2}$) and hydrogen-bonding interaction (δ_H MPa $^{1/2}$) [5,11]. Using these parameters, the relative solubility between two substances can be estimated based on the 'distance' between points in a three-dimensional coordinate system corresponding to the HSP in three-dimensional space. This distance is commonly referred to as "Hansen Space".

Although Hansen parameters are useful and provide information that quantifies the solubility properties of materials, the process involved in calculating these parameters for bitumen is laborious for routine measurements. A simpler and more practical method to determine the solubility tendencies and internal stabilities of different bitumens is based on an approach termed as the "bitumen solubility model" (BISOM), introduced by Redelius [5]. This model is a derivative of the HSP model and estimates the extent of the mutual solubility of bitumen molecules at different points in Hansen space. The calculations involved in BISOM are primarily based on the principles of turbidimetric titrations, which was initially used for the determination of asphaltene peptization of bitumen [12]. In this method, titrations are carried out for bitumen using titrants that have different orientations in Hansen space. Each titrant provides information about the solubility and internal stability, with respect to the strength of different molecular interactions between its molecules [13]. Mutually soluble and compatible bitumens would theoretically have comparable relative solubilities in Hansen space and exhibit comparative strength of intermolecular forces, such as dispersive force, hydrogen bonding and polar interactions [5]. Prior work has also shown that the rheological properties of binders such as relative viscosities can be correlated to the strength of the various interactions between their molecules [14]. Importantly, factors such as ageing are believed to affect the interactions and cause a decrease in the internal stability of binders [15].

However, this topic has not been well explored in literature yet. Many RAP binders are also markedly oxidized which may affect their compatibility for mixing with different unaged binders. Thus, it is hypothesized that the method of turbidimetric titrations using BISOM may be used to semi-quantitatively characterize the internal stability of aged RAP binders in comparison to unaged binders. Such results could potentially be used to evaluate the compatibility between binders and deliberate the recyclability of aged binders.

3. Scope

This study presents a simplified method to measure solubility-related parameters for aged and unaged binders based on the principles of turbidimetric titrations. Nine different binders were used to demonstrate the sensitivity of the technique and its ability to distinguish between different binders of varying ageing levels. Results from these measurements were further corroborated using Saturates, Aromatics, Resins and Asphaltene (SARA) fractionation of the binders. Overall, the work presented in this study was guided by the expectation that it would lead to a simplified metric to better understand the solubility and compatibility of different virgin-aged binder pairs. Future studies will be involved with evaluating the relationship of this metric with microstructures and long-term performance of binder pairs.

4. Materials

Nine binders from various sources were evaluated in this study, a typical unaged virgin binder of PG high-temperature grade of 64, four field aged binders extracted from different RAP sources labelled RAP-1, RAP-2, RAP-3 and RAP-4, and four laboratory aged binders named AARAP-1, AARAP-2, AARAP-3, AARAP-4. All RAP binders used in this study met the local specifications for reusability and were extracted from the RAP according to the procedure specified in AASHTO T164. The artificially aged binders were prepared from unaged binders of PG high-temperature grades of 58, 64, 70 and 76, using the rolling thin film oven (RTFO) method followed by the pressurized aging vessel (PAV) method as per standards AASHTO T 240– 09 and ASTM D 6521, respectively. All chemicals used in this study were of laboratory grade purchased from Thermo Fisher Scientific.

5. Experimental Methods and Procedure

5.1 Titration Procedure

The titration procedure followed in the study was based on the principle of turbidimetric titrations [13]. According to this principle, if two liquids with varying solubility parameters are reciprocally soluble, the solubility parameter of the whole mixture will be comparative to the amount of each liquid, which can be described by the following equation:

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

where ϕ is the volume fraction of each liquid i and j. Using this equation, the solubility property of a material can be calculated. Experimentally, the substance under investigation is titrated in solution using a non-solvent till precipitation ensues. In this study, 0.75 gms of bitumen was dissolved in 2 ml, 3 ml and 4 ml solutions of toluene in a closed flask to prepare three solutions of varying concentrations. The solutions were subsequently titrated with a non-solvent in 1 ml aliquots until flocculation was observed, which is the point of precipitation. Three different non-solvents were chosen for this study, namely iso-octane, 2-butanone and 2-ethyl-1-hexanol. These solvents were specifically chosen based on prior studies that calculated the HSP for bitumen, relating it to the various molecular interactions in the solubility model [5]. As the HSP represent the extent of interactions on three orthogonal scales, i.e., dispersive forces, polar interactions and hydrogen bonding, it is important to select a minimum of three solvents that demonstrate a diversity of magnitudes along each one of these three scales [5]. Table 1 shows the HSP of the solvent, non-solvents and bitumen. The HSP of bitumen is based on the average of 15 different binders as reported in literature [16]. Iso-octane, illustrative of the dispersive forces has low dispersive interaction and no polar or hydrogen bonding influences. 2-butanone indicative of the polar interactions has high polar interaction along with high dispersive forces and low hydrogen bonding. Lastly, 2-ethyl-1-hexanol indicative of the hydrogen bonding interactions has high dispersive and hydrogen bonding interactions but low polar interactions. The HSP points were plotted in a 3-D graph along with the HSP sphere of bitumen with radius 5.5 MPa^{½} as seen in Figure 1. The HSP sphere details the solubility of bitumen in Hansen space [17] and can be calculated using the following equation:

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

Where:
R_a=distance between a solvent and bitumen,
δ_{d1} (or δ_{p1} or δ_{h1}) = dispersion component of the solvent,
δ_{d1} (or δ_{p1} or δ_{h1}) = dispersion component of bitumen.

HSP of good solvents such as toluene fall close to the center of the solubility sphere of bitumen whereas those of poor solvents fall outside or close to the edge of the solubility sphere.

Table 1. HSP of Toluene, Titrants and Bitumen

	δ_D (MPa^{½})	δ_P (MPa^{½})	δ_H (MPa^{½})
Toluene	18	1.4	2
Iso-octane	14.3	0	0
2- butanone	16	9	5.1
2-ethyl-1- hexanol	16	3.3	11.9
Bitumen Avg.	18.6±0.3	3.9±0.2	3±0.2

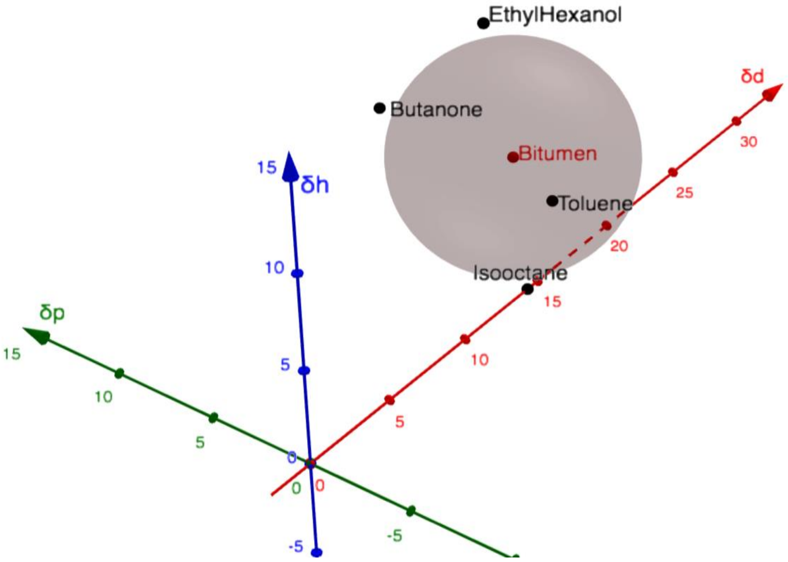

Figure 1. HSP of toluene and titrants in the HSP sphere of bitumen

As mentioned, the titration was conducted until flocculation occurred for each sample. Different methods have been reported to determine the point of flocculation for bitumen [18], such as placing a drop of solution on a filter paper and looking at the precipitate formed, examining a drop of solution through a microscope and automated methods using UV-spectrometers. This study adopted an improved version of the filter paper method to evaluate the point of flocculation. After the addition of each 1 mL aliquot of the titrant, a small drop was removed from the titration solution and placed on a filter paper. The procedure was continued after the addition of each aliquot until the formation of two distinct rings, which indicates the beginning of flocculation, was observed [12]. Figure 2 shows a sample image of a bitumen specimen and sequence of formed drops (from left to right) after the addition of each aliquot of non-solvent until flocculation occurred as an example. The total volume of titrant added at the flocculation point was noted.

Figure 2. Images on filter paper after the addition of each aliquot of titrant (left to right)

Although the exact point of flocculation can be detected by eye at the concentrations and volumes used in this work, the results of each titration were corroborated using image analysis with MATLAB to eliminate any bias that may be introduced. The analysis algorithm calculated the difference in colour intensities as one transverse from the center of the circular drop to the outer edge using the Image Processing Toolbox^{TM}. Through trial and error, and validation of the results with the flocculation point detected by eye, a difference of above 30% between the intensity of the inner core and the outer annular ring was set as the point of flocculation. Figure 3 shows a sample calculation using the analysis method. The use of filter paper with simplified image analysis can be a potential approach in the future to expand this method in a manner that is easy to perform, objective and repeatable.

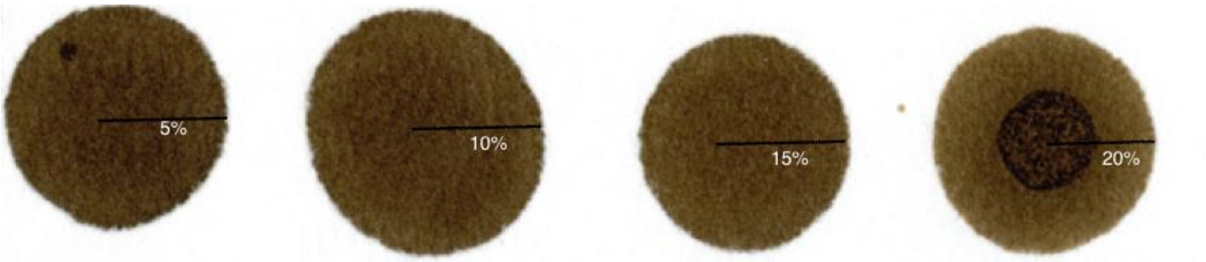

Figure 3. Colour intensity analysis of titration results

After determining the flocculation point for each titration, two parameters, namely flocculation ratio (FR) and concentration (C), were calculated using the following equations [18]:

$$FR = \frac{V_S}{V_S + V_T}$$

$$C = \frac{W_A}{V_S + V_T}$$

Where V_S is the volume of solvent, V_T is the volume of titrant and W_A is the weight of bitumen. The values for FR and C at each of the three bitumen concentrations were plotted on a graph. A linear regression was conducted through the precipitation points and the straight line was extrapolated to cross the x and y axes. The intercepts were denoted as FR_{max} and C_{min} for the corresponding axes. FR_{max} is regarded to be related to the peptizability of the least soluble components in bitumen whereas Cmin is related to the stability of the respective bitumen [7]. Figure 4 illustrates the extrapolation technique.

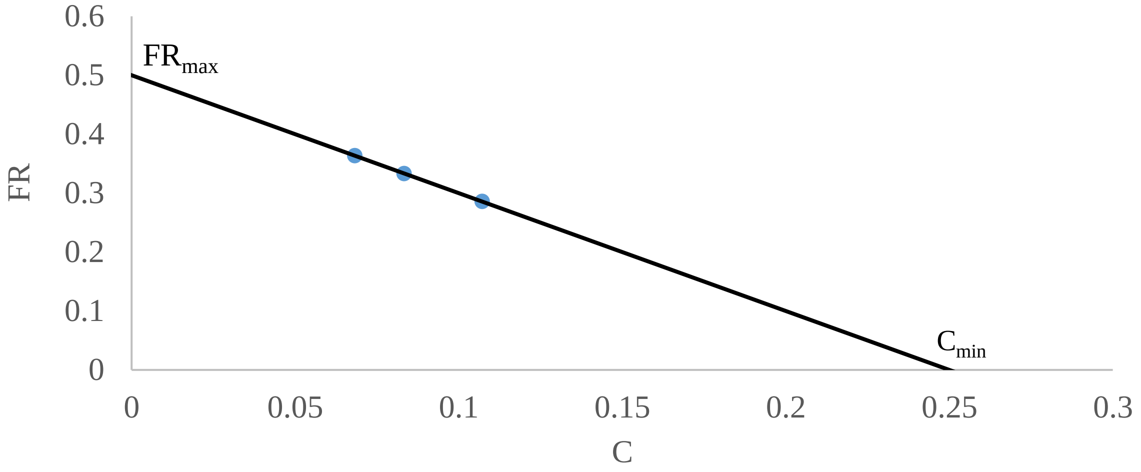

Figure 4. Extrapolated graph of FR vs C

Following this, further calculations were conducted to obtain the solubility related parameters of bitumen for the different binders used in this study. The letters in the following equations were designated by the type of interaction as follows: dispersive interactions with iso-octane were termed with the letter D, polar forces with 2-butanone were termed with the letter N, and hydrogen bonding interactions with 2-ethyl-hexanol were termed with the letter H. The parameter D_a (or N_a or H_a) was calculated as follows:

$$D_a = 1 - FR_{max}$$

This parameter specifies the solubility of the most insoluble molecules in bitumen. The next parameter D_0 (N_0 or H_0), denoting the solubility power of bitumen, was calculated by:

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

Finally, parameter D (or N or H) was calculated as shown below. This parameter gives an indication of the internal stability of a bitumen sample:

$$D = \frac{D_0}{1 - D_a}$$

As the bitumen was titrated with titrants having distinctive solubility parameters concerning the three types of molecular interactions in the HSP Model, the parameter D (or N or H) gives the stability of bitumen in these different solvents. Therefore, this parameter D (or N or H) also serves by extension as an indicator of the relative strength of the respective interaction in it. Nevertheless, it must be emphasized that the parameters N and H do not exclusively indicate the polar and hydrogen bonding-driven interactions, since the selected solvents were not solely polar or hydrogen bond-driven. Rather, these terms would indicate more polar or hydrogen bond leaning solubility tendencies.

5.2 Saturates, Aromatics, Resins and Asphaltene (SARA) Fractionation

The SARA fractionations of the various bitumen samples were conducted using a method described in a previous work [19]. This method was mainly divided into two parts. The first part was the solubility-based separation of asphaltenes and extraction of maltenes. The second part was chromatography-based separation of the maltenes fraction into saturates, aromatics and resins. A small amount of bitumen was first dissolved in n-heptane by stirring at room temperature. The undissolved asphaltene was filtered using PTFE-based syringe filters of pore size of 0.2 μm. This method of asphaletne-maltene filtration is known to separate higher amounts of asphaltenes compared with other conventional methods, which is important in the context of this work. The separated maltene (in the n-heptane solution) was then applied on a solid phase extraction (SPE) cartridge which contains silica gel. In three steps, in increasing order of polarity, three solvents namely n-heptane, toluene and dichloromethane were used to elute the three maltene-based fractions of bitumen. The solvents are pushed through SPE cartridges by action of gravity and vacuum. Figure 5 shows a sample elution of the aromatics fraction through SPE cartridges at three different phases.

Figure 5. Elution of aromatics through SPE cartridges [19]

6. Results and Discussion

6.1 Internal Stability and Intermolecular Interactions

The various parameters corresponding to the dispersive, polar and hydrogen bonding interactions were calculated as explained in the previous section. The results for D, H and N are presented as “triangles” in Figure 6 (RAP binders and virgin binder) and Figure 7 (PAV aged binder and virgin binder). First, it is important to understand the premise and concept of intermolecular interactions in bitumen. Bitumen can be described as a complex mixture of molecules with varying molecular weights that are dependent on the source and individual chemistry of any given binder. The molecules in this mixture relate with one another through various intermolecular interactions and associations as described earlier. An indication of the stability of these molecules as a colloid or a dispersed phase, and relative strength of these interactions are represented by the D, H and N parameters shown in the figures.

6.1.1 Dispersive Forces

Based on the results presented, one substantial difference between the unaged binder and aged binders are the dispersive forces. Previous research has indicated binders exhibiting low values of D, of close to 2, such as some of the aged binders seen in this study may exhibit low peptizability and could be thermodynamically unstable, hence making it unsuitable to be reused [5]. The dispersive interactions in bitumen can also be derived mathematically from electronic polarizability and refractivity using the following equation [14]:

$$\alpha = \left(\frac{3}{4\pi N_A}\right)\left(\frac{M}{d}\right)\left(\frac{n^2-1}{n^2+2}\right)$$

Where,
N_A = Avogadro’s number,
M = Molecular weight,
d = Density and
n = Refractive Index.

These interactions are also often termed as “London Forces” and are a consequence of temporary dipoles due to fluctuations of electrons around a molecule. Dispersive forces are generally considered as a weak intermolecular interaction. However, it has been reported to be an important form of interaction between molecules in bitumen that determines its physical properties [14].

6.1.2 Polar and Hydrogen Bonding Interactions

The most substantial difference between aged and unaged binders in terms of intermolecular forces is polar interactions, which the authors believe could play a significant role in the mobilisation and blending of RAP binder. The extents of polar interactions exhibited by the aged binders were noticeably different as compared to the unaged binder. This difference was more discernible in the field aged RAP as compared to the artificially aged binder. This may be due to the fact that some of the artificially aged binders were polymer modified, and PAV ageing may not accurately simulate the ageing that occurs in field, especially in terms of UV ageing, which has been shown to appreciably alter the chemistry of binders in terms of polarity [20].

At the molecular level, polarity is the separation of charge within a molecule. All of the naturally occurring heteroatoms, such as nitrogen, sulfur, and oxygen, contribute to bitumen polarity. Upon ageing, the oxidation products formed are polar and further contribute to the overall polarity of the system [21]. The extent of hydrogen bonding also showed similar trends as the polar interactions as it is also mainly based on the content of more electronegative elements such as oxygen and nitrogen. At the intermolecular level, a critical aspect of polar molecules is the attraction towards each other as a result of their separated charges, forming chains of interaction. These can be illustrated using simple schematic diagrams as shown in Figure 8 [22]. The association of these molecules to their most stable thermodynamic state is a combination of electrostatic and other short-range forces. With ageing, the freshly oxidized sites have a pronounced effect on polarity and newer associations are formed in larger number than the original binder. The rates of these associations depend upon the number of sites and the magnitudes of the attractions. The stronger the attractions, the greater the driving forces to associate. It is evident that the increase in polarity affects the mobility of molecules, and can create immobilization of polar components through molecular agglomeration, thereby affecting other intermolecular associations, such as molecular dispersion [21]. When considering the mixing of aged binders and virgin binders in RAP mixing, the possible increased associations could have a significant effect in terms of blending and stability of the combined binders. This will be discussed in detail in the next sections.

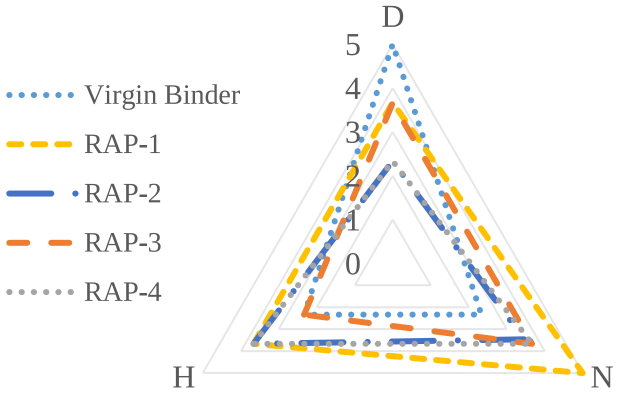

Figure 6. Strength of intermolecular interactions in RAP binders and virgin binder

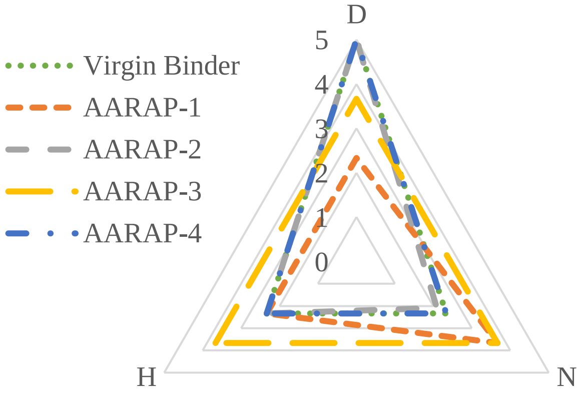

Figure 7. Strength of intermolecular interactions in artificially aged binders and virgin binder

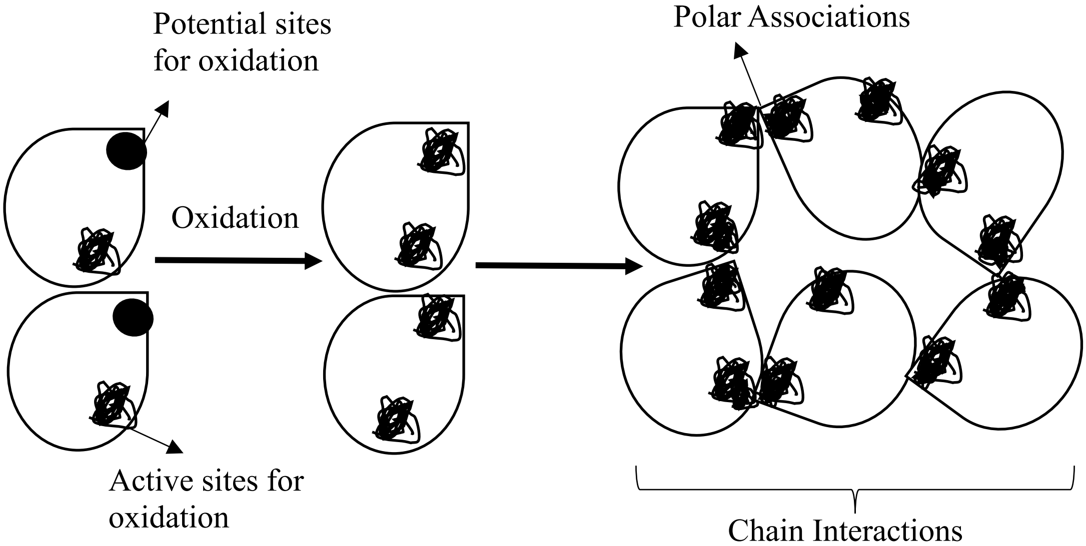

Figure 8. Polar associations between molecules

6.2 Implications of Intermolecular Forces on RAP Binder Mobilisation

One of the considerations in the design of mixtures with RAP is the availability of aged binder from RAP. Many studies have investigated the performance of mixed blends through the mechanical mixing of unaged and aged binders [23]. Although this is useful to understand the basic rheology of combined binders, the actual mixing process is far more complex, and the question remains as to whether or not such blends are compatible and consequentially stable over long periods of time.

As the aged binder exists as a layer covering RAP aggregates, a better hypothesis of this, is the blending achieved though mechanical mixing and molecular diffusion driven by energy imbalances and polar attractions. Most studies have indicated that there is partial mobilisation and blending of RAP binder during the mixing process [4,24]. Further, the extent of this mobilisation has been shown to be variable dependent on other factors. These factors can be broadly classified as extrinsic, such as mixing temperature, retention time at mixing temperature and mixing method, and intrinsic to the material, such as mutual compatibility of the RAP binder and virgin binder [3]. Extrinsic factors, such as temperature and retention time, can increase the extent of interaction between aged and unaged binders. Specifically, high temperatures can increase molecular mobility and retention times can allow molecules to further interact with each other. However, it is the combination of the extrinsic with the intrinsic factors that dictates the extent to which the aged binder is activated, mobilised and blended with the virgin binder. Furthermore, mere blending of aged RAP and virgin binder facilitated by extrinsic factors does not necessarily imply that the final blend is homogenous and stable in the long term. This degree of blending would be governed by an inter-diffusion process wherein the aged and virgin binder would diffuse into each other at a molecular level [25]. The level of the intermolecular agglomeration and strengths of molecular interactions will affect the level of diffusion and long-term stability of the blend.

Considering this, highly aged RAP binders would need to be mixed with chemically compatible virgin binders with special mixing conditions like higher temperature and mixing time in order to mobilise it and achieve a homogenous blend. Nonetheless, there are currently no specifications that define the compatibility of aged and unaged bitumens. Furthermore, it is now common that additives, such as warm mix additives and rejuvenators, are used in RAP mixtures. The effects of these additives on unaged-aged binder compatibility should also be investigated.

6.3 SARA Fractionation

The SARA fractions of the various binders were determined as per the method described and the results are presented in Figure 9. Although the original sources of bitumen were different for different binders, the SARA fractions can still provide useful information regarding their chemical nature and polarity-based tendencies. The two often opposing models of bitumen are based on the "colloidal model" and the "dispersed fluid model" respectively, and their perceived differences in microstructure are already well established in literature [26]. However, when considering the polarity-based fractions, i.e., SARA fractions, these models are not contradictory, with each model having its respective application. Through the polar fractions, bitumen can be modelled as a discretization of a chemical continuum with gradual increase of polarity. Using the titration method in this study, which is based on a dispersed fluid model, the total polarity distribution of each bitumen as a whole can be gauged, whereas the SARA fractions can quantify the different polar fractions in it. The extent of these fractions will naturally affect the overall intermolecular interactions and internal stability of each bitumen. Moreover, SARA fractionation is also a well-developed practice and its correlation with blending of different bitumens is established [26].

The ranking of bitumen fractions by increase in polarity is saturates, aromatics, resins and asphaltenes. The ageing of bitumen generally first leads to a decline in aromatic content and subsequent increase in resin and asphaltene contents. It is hypothesised that the aromatics generate resins which are then converted into asphaltenes. Studies have shown that the asphaltene content could be the controlling factor that determines the overall solubility of a bitumen system [27]. When considering the SARA fractions for the various binders, the highest asphaltene content was observed for the field aged RAP binders, followed by the artificially aged binders and virgin binders. The asphaltene contents calculated using this method usually range from 15%-20 % for unaged binders to 25% -35% for PAV aged and field aged binders [19]. Asphaltene and resin fractions are known to possess heteroatoms that are strongly linked with polar functional groups. Hence, their increase is known to increase the overall polarity in bitumen.

Further, it has been reported that aged binders can possess amplified molecular clustering due to increased polar associations, and aromatization of reactive compounds which make bitumens more planar and susceptible to asphaltene agglomeration [28]. Studies on the binder energies for unoxidised and oxidized asphaltene dimers have shown that the total values of intermolecular interactions are stronger for oxidized forms as opposed to unoxidised forms, and hence expected to increase agglomerations, leading to the hardening of bitumen [29]. The effect of these increased agglomerations when considering mixing aged binders with unaged binders is a relevant influence that needs to be deliberated.

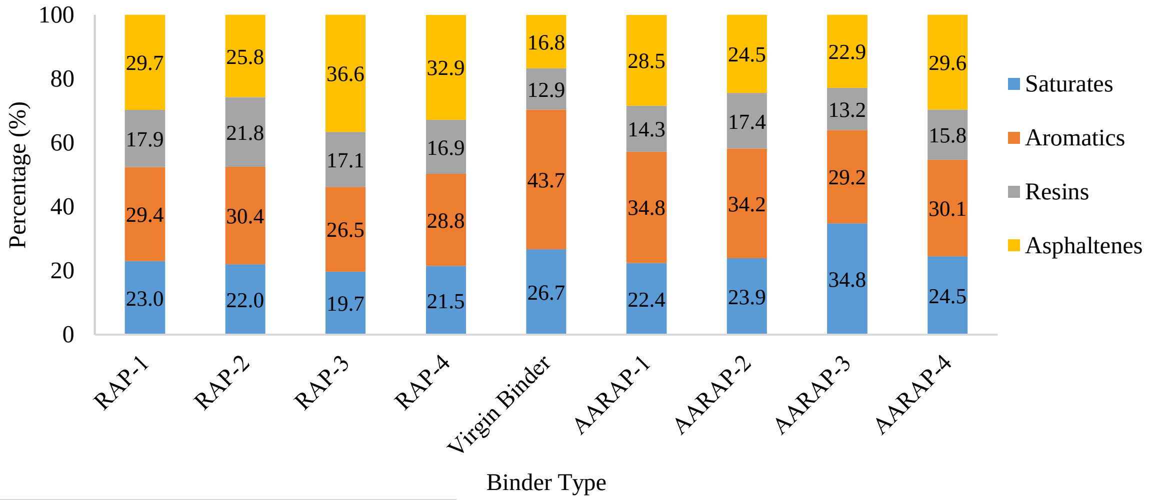

Figure 9. SARA fractions of binders.

6.4 Influence of Polarity and Solubility on Virgin-RAP Binder Blends

From the results obtained through the BISOM parameters and SARA fractionation, it can be seen that aged binders and virgin binders are fundamentally different in terms of intermolecular interactions and chemical composition. These differences are consistent with the broad understanding of the materials established in literature. When considering the mixing of different bitumens, it is hypothesized that compatibility between them would be dictated by the mutual solubility of an assortment of components, each having varying solvating powers [30]. Solubility of bitumen blends would be dependent on the force of attraction and repulsion within and around the molecules in the blend. Relating it to the solubility parameters, a bitumen blend can be considered to be well dispersed and stable when all contributing portions have similar solubility parameters. The underlying concept around this being the correlation between cohesive energy density and mutual miscibility [31]. Cohesive energy density is described as the energy that holds bitumen molecules together, and its measure in each bitumen is dependent on the various intermolecular forces.

Oxidation of bitumen greatly affects the interaction energy between molecules and hence the cohesive energy density. Increased cohesive energy densities are correlated to increased molecular agglomeration and consequently a probable increase in polarity [31]. In a stable and well dispersed bitumen, a delicate balance would exist between its various agglomerated and dispersing components. When considering the effect of introducing a component with a higher polarity into the bitumen blend such as during the mixing of RAP binders with virgin binders, depending on the strength of the intermolecular force, it may exhibit a governing influence on the overall molecular interactions leading to variability in properties of the blend. Consequently, in a bitumen blend with RAP, to obtain sufficient solvency of the increased fractions with higher polarity, the solvency power of the maltenes must be comparable to fully disperse them. If not, it is possible that blended mixtures could have heterogeneous components that are insufficiently dispersed to achieve a stable binder, displaying peculiar rheological behaviour.

An indication of this phenomenon is the reported literature regarding the unpredictability in properties of cross blended asphalt binders [32]. Viscosities of asphalt mixtures of blends have shown irregularities when compared with the viscosities of the original asphalts. These irregularities usually occur when one of the bitumen contains a large concentration of high molecular weight asphaltenes and the other bitumen has a maltene phase of solvent power different from that of the first bitumen. The change in maltene solvent power then causes a change in the degree of aggregation of the high molecular weight asphaltenes in the mixture. Further, it has also been shown that asphaltenes from different sources had different effects of blend rheology when added to the same maltene fraction. With the increase in oxidation and overall molecular agglomeration of RAP binders, this effect could be accentuated, resulting in blended bitumens that may not be fully solvated.

In order to achieve a stable blend at different RAP proportions, the RAP binder would need to be the mixed with sufficiently solvable bitumens. This is preferably achieved on an individual basis as although different RAP binders may exhibit similar rheological characteristics, they may be different in chemical compositions [30]. It can be expected that methods such as the BISOM titration procedure could be useful to indicate such intrinsic differences between blended binders, considering most current specifications on RAP mixture design are insufficient as they are often simplistic and calculate blend composition based on some parameters such as penetration and PG grading [1]. Although this may be acceptable for low RAP contents, for high RAP mixes, this can lead to poor quality and incompatible bitumen prone to premature failure. Hence, a more comprehensive approach considering binder chemistries is suggested, and a detailed framework for evaluating compatibility between aged and virgin binders needs to be defined in order to design RAP mixes.

7. Findings and Conclusion

In this study, the compatibilities between new and aged binders were evaluated in terms of intermolecular interactions using an extension of the HSP model of solubility. The following findings and conclusions could be drawn from the laboratory tests:

- The turbidimetric titration method using the selected titrants effectively detected the differences between aged and unaged binders in terms of internal stability and molecular interactions.
- The analysis of the titration results indicated that the most notable differences between unaged and aged binders were in terms of polar interactions and dispersive forces. These differences were consistent with the existing understanding of the nature of aged binders.

- These results were validated through SARA fractionation, implying that the greater asphaltene content of the aged binders could significantly contribute to the extent of polar interactions in them, providing additional validation for the proposed procedure.
- Different virgin-aged binder pairs showed different extents of similarity based on the solubility parameters calculated, and consequently are expected to have different extents of mutual compatibility.
- It is likely that a stable blend of virgin and aged binder can be achieved if the solvency power of the virgin binders can full disperse the molecular agglomeration in the aged binder.
- Special mixing conditions such as increased temperature and mixing conditions may improve the relative compatibility between binders, in relation to aged binder mobilisation and blending. However, its effect on long term performance needs to be further evaluated.
- A limitation of this study was that the titration procedure adopted can only indicate the relative differences with respect to the various intermolecular interactions in the bitumens tested. An automated titration procedure may be adopted for a more precise measurement of the different solubility-based parameters.

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