FUNDAMENTAL AND COMPREHENSIVE CHARACTERIZATION OF THE MOBILISATION AND BLENDING OF AGED AND UNAGED BINDERS IN RECLAIMED ASPHALT PAVEMENT (RAP) MIXTURES

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A thesis submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

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CERTIFICATE OF ORIGINALITY

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ABSTRACT

The use of reclaimed asphalt pavement (RAP) in new bituminous mixtures has become a routine practice in many parts of the world as it is known to provide considerable environmental and economic benefits. However, the mixture design associated with it is complicated, with one of the concerns being the attributes of the resulting binder that is formed in the mix. Specifically, asphalt binders in mixtures with RAP consist of segments of both aged (RAP binder) and unaged (virgin) binders, intended to exist as a single entity. A significant apprehension in the design of such mixes is the undetermined extent of aged binder that is mobilised during mixing, and the ensuing blending of aged and unaged binders. The level of this blending is theorized to control the extent of homogeneity of the binder in the mix, and consequently has an important role in the overall mixture performance. This dissertation research is concerned with systematically investigating and improving the fundamental understanding of the many facets involved in the mobilisation of RAP binder and the subsequent interaction of RAP binders and unaged binders.

The first part of this dissertation was focused on developing a novel technique to evaluate RAP binder mobilisation using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) as a major assessment tool. Following this, the effects of important variables in mixture design such as mixing temperature, incorporation of warm mix asphalt (WMA) additives and different RAP materials were assessed. Chemical tests such as saturates, aromatics, resin and asphaltenes (SARA) fractionation and microstructural analysis using optical microscopic techniques were then used to concurrently identify the possible mechanisms dictating the mobilisation process. The analysis results suggested that RAP binder mobilisation is greatly dependent on the mixing temperature, and the inclusion of certain WMA additives will also influence the extent of mobilisation. Moreover, the degrees of mobilisation were seen to vary based on the specific type of RAP used in the mix. Based on these results, it was proposed that viscosity could be a useful parameter for practitioners to assess and standardize RAP variability.

In the second part, the compatibilities between unaged and aged binders were studied to fully capture the interaction mechanism of binders in RAP mixtures. An extension of the Hansen solubility parameter (HSP) model of solubility was used to approximate the relative molecular interactions of binders in terms of dispersive interactions, hydrogen bonding interactions and polar interactions. It was seen that some unaged binders and aged binders could markedly vary in terms of certain molecular interactions. This, in turn, is expected to have compatibility-based implications for the mobilisation of RAP binder and its blending with unaged binders. An investigation was also conducted into the chemistry and internal stability of combined blends of RAP binder and unaged binder. It was observed that higher concentrations of aged binders incorporated into unaged binders could change the internal stability of the blends, and plausibly affect the polydispersity of molecules. Hence, some consideration of the characteristics of the intermixing binders could be essential to design the most appropriate mix.

LIST OF PUBLICATIONS

Journal Papers (Published)

- **A Sreeram**, Z Leng, R Hajj, A Bhasin (2019). Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility, *Fuel*, DOI: 10.1016/j.fuel.2019.05.161.
- **A Sreeram**, Z Leng (2019). Variability of RAP binder mobilisation in hot mix asphalt mixtures*, Construction and Building Materials* 201, 502-509.
- **A Sreeram**, Z Leng, Y Zhang, RK Padhan (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.
- Z Leng, **A Sreeram**, RK Padhan, Z Tan (2018). Value-added application of waste PET based additives in bituminous mixtures containing high percentage of reclaimed asphalt pavement (RAP), *Journal of Cleaner Production* 196, 615-625.
- **A Sreeram**, Z Leng, RK Padhan, X Qu (2019). Eco-friendly paving materials using waste PET and reclaimed asphalt pavement, *HKIE Transaction*s 25:4, 237-247.

Journal Papers (Under Review)

- **A Sreeram,** Z Leng, R Hajj, L Ferreira, Z Tan, A Bhasin. Fundamental Investigation of the Interaction Mechanism between New and Aged Binders in Binder Blends, Submitted to the *International Journal of Pavement Engineering.*

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LIST OF ABBREVIATIONS

RAP	Reclaimed Asphalt Pavement
ATR	Attenuated Total Reflectance
FTIR	Fourier Transform Infrared (ATR-FTIR) Spectroscopy
WMA	Warm Mix Additives
SARA	Saturates, Aromatics, Resins, Asphaltenes
HSP	Hansen Solubility Parameters
GPC	Gel Permeation Chromatography
HMA	Hot Mix Asphalt
DOT	Department of Transport
C&D	Construction and Demolition
SMA	Stone Mastic Asphalt
OGA	Open Graded Asphalt
PG	Performance Grading
TSR	Tensile strength ratio
IR	Infra-Red
NMR	Nuclear Magnetic Resonance
SHRP	Strategic Highway Research Program
AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials

BISOM	Bitumen Solubility Model
AFM	Atomic Force Microscopy
BBR	Bending Beam rheometer
RTFOT	Rolling Thin Film Oven Test
PAV	Pressurised Ageing Vessel
UV	Ultraviolet
DSC	Differential Scanning Calorimeter
IA	Integrated Area
TCE	Trichloroethylene
LMS	Large Molecular Size
MMS	Medium molecular Size
SMS	Small molecular size
THF	Tetrahydrofuran
PTFE	Polytetrafluoroethylene
SPE	Solid Phase Extraction
FAM	Fine Aggregate Matrix
MD	Molecular Dynamics

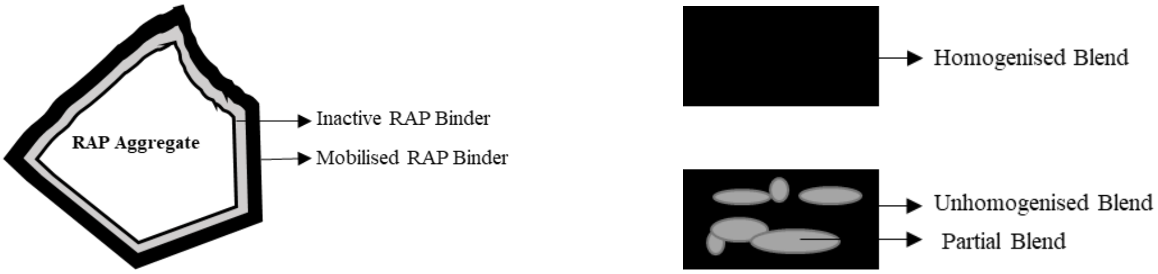
CHAPTER 1

INTRODUCTION

1.1 Background

The construction of pavements is progressively moving towards the incorporation of eco-friendlier and sustainable practices intended to decrease the overall environmental impact in terms of carbon footprint and energy expenditure. The utilisation of reclaimed asphalt pavement (RAP) in new bituminous mixtures is one such measure and shown to provide considerable environmental and economic benefits [1]. However, from an engineering perspective, many concerns still persist regarding the unpredictable performance of RAP mixtures and uncertain elements in RAP mixture design [2]. One of the main apprehensions hindering the applicability of high RAP mixtures is the ambiguity regarding the extent of aged binder covering RAP aggregates, referred to as "RAP binder" that is mobilised during mixture production. Consequentially, some proportion of this RAP binder is expected to be accessible to be blended with the unaged (virgin) binder, to form a combined binder layer around aggregates in the mixture.

The earliest theories around RAP binder mobilisation and blending assumed that the RAP binder mixes with the virgin binder to create a new blend with target properties [1]. It was believed that during mixture production, all the RAP binder covering RAP aggregates could be utilized and blends with the virgin binder. This is now commonly believed to be an oversimplification and consequently, the real extent of the mobilisation of RAP binder and blending between aged and unaged binders have been a matter of much deliberation among researchers. The mobilisation and blending phenomenon are illustrated in Figure 1.1 which explains the existence of an activated or mobilised layer of binder around RAP aggregates during mixture production. The mobilised binder then blends with the virgin binder to some degree during this production process [3]. Another effect that had been earlier considered was the “black rock” effect which suggests the possibility of a double coat of aged and unaged binder on RAP aggregates when RAP is used [4]. Due to these uncertainties and variability involved, many regulatory frameworks specify caution when determining targets for the blending of binders in RAP mixtures [5].



a) Mobilised RAP Binder b) Blending Scenario

Figure 1.1 Mobilisation and Blending Phenomenon in RAP Mixtures

The phenomenon of RAP binder mobilisation and blending (of aged and unaged binders) have been studied by investigators in the past using various rheological and chemical techniques [6, 7]. Some researchers have used rheological approaches and models to predict the dynamic modulus |E*| of blended binders extracted from recycled mixtures, through matching their master curves of dynamic modulus measured in the laboratory [8,9]. Regarding chemical methods, gel permeation chromatography (GPC) and Fourier transform Infra-Red (FTIR) spectroscopy have been the main tools used for assessment. Overall, RAP binder mobilisation and blending is a critical design issue as under-asphalted mixtures arising from low mobilisation and blending levels can significantly increase the possibility of fatigue cracking and moisture damage in mixtures [1]. In terms of existing research, there is no tangible consensus regarding RAP binder mobilisation and blending of binders, and there exists an imperative need to validate prior results using varied methods under different laboratory conditions. Significantly, a basic understanding regarding the mechanism of mobilisation and subsequent interaction between aged and unaged binders is lacking and needs to be investigated.

This dissertation research is concerned with systematically examining and improving the fundamental understanding regarding the various facets involved in the mobilisation of RAP binder and the ensuing blending of RAP binder and unaged binders. In the first part of the study, experiments were devised and performed to evaluate RAP binder mobilisation and blending efficiency using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy as a major assessment tool. Following this, the effect of important variables in mixture design and probable mechanisms involved in the mobilisation process were investigated. In the second part, the compatibilities between aged and unaged binders, and the internal stability of combined blends of these binders were assessed, primarily using an extension of the Hansen solubility parameter (HSP) model of solubility.

1.2 Research Objective and Scope

The objective of this dissertation is to systematically investigate and advance the fundamental understanding regarding the various features involved in the mobilisation and blending of RAP binders with virgin binders in asphalt mixtures. To achieve this objective, the following research tasks were conducted:

- A comprehensive literature review concerning the utilisation and performance properties of RAP; mobilisation and blending of binders in RAP mixtures; the chemistry of binders and combined blends.
- Design of an experimental method to determine the extent of RAP binder mobilisation and blending efficiency using ATR-FTIR as a method of evaluation.
- Validation of the proposed method using chemical and rheological analysis.

- Investigation of the effect of important variables in mixture design such as mixing temperature, WMA additives, and RAP type.
- Deduction of the probable mechanism of mobilisation using chemical and microscopical analysis.
- Evaluation of the compatibility between unaged and aged binders using a solubility-based model, and its effect on RAP binder mobilisation and blending of unaged and aged binders.
- Study on the interaction mechanism between unaged and aged binders in binder blends.

1.3 Significance of this Research

The original contributions of the dissertations are listed as follows:

- Development of a novel method to determine the extent of RAP binder mobilisation and blending efficiency in bituminous mixtures using ATR-FTIR.
- Investigation of the effects of different mix variables in RAP mixture design, and the deduction of the probable mechanisms that dictate RAP binder mobilisation.
- Insight on the compatibilities between aged and unaged binders, and its effect on the mobilisation and blending phenomenon.
- Evaluation of the distinctive chemistry and internal stability of binder blends composed of aged and unaged binder.

1.4 Organisation of this Dissertation

As per the scope of the research listed above, this dissertation is divided into 7 chapters:

- Chapter 1 presents the general background and organisational structure of this dissertation.
- Chapter 2 presents a literature review regarding 1) the current global status of RAP use in asphalt pavements 2) performance properties and major challenges in the design of

RAP mixtures 3) prior findings regarding the blending and mobilisation of binders 4) chemistry and rheology of binders and binder blends.

- Chapter 3 presents a method to evaluate RAP binder mobilisation and blending efficiency, including validation of the proposed method using chemical and rheological analyses.
- Chapter 4 is divided into two parts. Part A presents the effect of using different WMA additives on RAP binder mobilisation. Part B assesses the effect of using different RAP materials on the same phenomena. The probable mechanisms dictating the results obtained are also deliberated using chemical and microscopical techniques.
- Chapter 5 presents an investigation into the compatibility between aged and unaged binders using a solubility-based model, and its effect on RAP binder mobilisation and blending.
- Chapter 6 characterises the chemistry and internal stability of combined blends composed of aged and unaged binders.
- Chapter 7 summarises the findings and conclusions from the study and the recommendations for future work.

The overall research framework of this dissertation is presented in Figure 1.2.

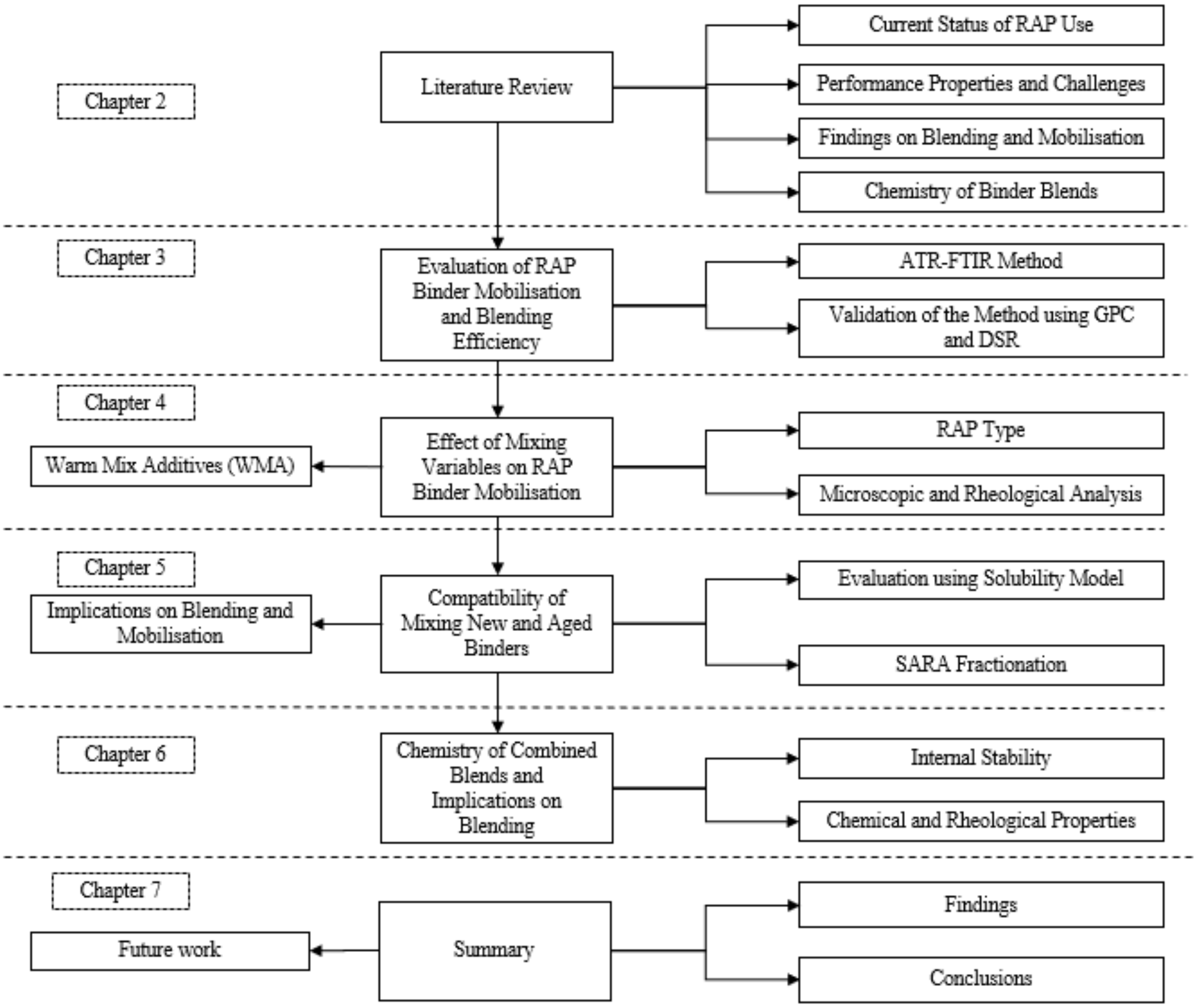


Figure 1.2 Research Framework

CHAPTER 2

LITERATURE REVIEW

The recycling of asphalt pavement in the form of reclaimed asphalt pavement (RAP) has become a widespread custom in the highway and pavement sector. In this chapter, the recent developments related to RAP research is presented including background regarding RAP materials; the present standing of RAP use worldwide; mix design and rheological properties of mixtures comprising RAP; research on RAP binder mobilisation and blending efficiency which is the principal focus of this dissertation and lastly the chemistry of unaged binders, aged binders and binder blends.

Portions of the discussion presented in this chapter have been previously published in "Evaluation of RAP binder mobilisation and blending efficiency in bituminous mixtures: An approach using ATR-FTIR and artificial aggregate, Construction and Building Materials 179 (2018), 245-253"; "Variability of RAP binder mobilisation in hot mix asphalt mixtures, Construction and Building Materials 201 (2019), 502-509"; " Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility, Fuel, DOI: 10.1016/j.fuel.2019.05.161"

2.1 Overview

The combination of asphalt binder and aggregate acquired as a result of recycling typically hot mix asphalt (HMA) is designated as reclaimed asphalt pavement (RAP). The utilisation of RAP in asphalt mixtures has become a necessity in many parts of the world due to the increasing price of bitumen, the shortage of quality aggregates and the need to embrace more sustainable methods in each sector of the environment [10]. Studies in the past have reported savings of up to 34% when RAP content between 20 to 50% was used in terms of material and construction costs [11]. Nevertheless, this is thought to be a good indicator but may not necessarily reflect the real savings in terms of the overall life cycle of the pavement. Further, it is acknowledged by practitioners that the utilisation of the highest proportions of RAP should be conducted with a general view of designing an economical and high-quality mixture, comparable to performance as 100 % virgin mixes.

2.2 RAP Use Worldwide

In view of economic considerations and environmental concerns, many transport and highway departments around the world have attempted using RAP in new bituminous mixtures with different levels of success and popularity.

2.2.1 Hong Kong

As of the writing of this dissertation, the maximum amount of RAP allowed in new bituminous mixtures is 30% and there are ongoing studies to increase this percentage [12]. However, in general, the use of RAP is not a popular approach among contractors mainly due to logistical concerns.

2.2.2 United States of America (USA)

In the USA, the quantity of RAP utilised in new mixtures was normally less than 15% as there was not a considerable advantage of using a larger percentage of RAP. However, around the year 2008, there was a notable increase in the price of bitumen and an overall decrease in supplies. Henceforth, the usage of RAP in new mixtures became popular again among practitioners. As of 2011, the yearly production of new asphaltic materials in the United States was close to 500 million tons, which comprised about 60 million tons of RAP material [4]. As the rate of recycling is high for all asphalt material, it has the greatest reuse rate by proportion among all recycled materials in the United States. Most State Departments of Transportations (DOTs) have stated that the utilisation of RAP is largely steered by the overheads of raw materials and transportation. However, most states reported that they did not exclusively track the percentages of RAP used or the overall cost savings. The main reason for this is that HMA is not tendered based on its constituents, on the contrary, it is tendered as a material on its own.

The most extensive survey done in the US with regard to RAP specifications was conducted by the North Carolina Department of Transportation with backing from the AASHTO sub-committee on materials [13]. Surveys were used from the 50 states in the USA, and the State of Ontario in Canada, which advocated that the bulk of the DOT specifications permitted for the utilisation of RAP in HMA. In addition, the mean national usage rate was determined to be around 12%. The maximum RAP usage was reported in the states of Florida and Michigan of around 30% and minimum usage rates were reported in the states of Wyoming and Arizona of less than 5%. Another review was performed by the Materials Engineering and Research Office of the Ministry of Transportation of Ontario, Canada, which corroborated the findings from the NCDOT survey from 2007 [14]. This study reported that 20-30% of RAP was commonly allowed for binder and base courses. Additionally, it was stated that the permitted proportion of RAP was larger for light traffic roadways and base courses, in contrast to medium or heavy traffic roadways. Later on, in 2009, a comparable survey was conducted by NCDOT, which showed that half of the states improved on their overall RAP usage from 2007 to 2009 [15]. Many State DOTs testified on trialling with or regularly using high RAP percentages, although it was not a general practice. According to the survey, many State DOTs permitted the usage of above 25% RAP in HMA layers, even though less than half of the states actually used greater 20% RAP in HMA layers. Most of the State DOTs also mandated that mixtures using RAP also meet other conventional mix design requirements. Other conditions commonly included the grade of the asphalt binder, type of aggregate used and size of nominal maximum aggregate. Interestingly, another survey by the Ohio DOT (ODOT) indicated that there were no distinct requirements for high RAP mixtures outside the design process for conventional mixes [16]. Since 2009, the change in the total percentage of RAP use by all sectors had increased steadily at a rate of about 1% per year. The survey also indicated that the number of states reporting average RAP percentages greater than 20% also increased significantly, rising from 14 states in 2009 to 27 states in 2014. Lastly, the number of states reporting RAP percentages of less than 15% decreased from 19 states in 2009 to 9 states in 2014. The states of Nebraska, Florida, and Michigan reported high RAP use of more than 30% with most states reporting the use of around 15-30%.

2.2.3 Japan

As per existing literature, mixtures with a high proportion of RAP are more widely produced in Japan than any other part of the world. It is reckoned that the standard amount of RAP used in a pavement in Japan is around 47%. More than 80.6 million vehicles commute in the roadways in Japan and about 791,189 miles of roads in Japan are owned privately [17]. Japan produces around 55 million tonnes of HMA yearly and has about 1150 asphalt plants serving the majority of the country. Out of the HMA produced yearly, nearly 41.9 million of it contain RAP [18]. Japanese asphalt plants are mostly batch-type which produces smaller quantities with lower production rates as compared to other countries. It is estimated that about 15% of HMA mixtures in Japan use polymer-modified asphalt binders. The roadways in Japan are considerably mature and hence the paving is mostly for maintenance-related works and surface courses. The contractors in Japan generally place importance on safety and have a pressing commitment to recycling. National laws also dictate the utilisation of RAP in pavement applications i.e. the Waste Management and Public Cleansing Law (Law No. 137 of 1970) and the act on Promotion of Procurement of Eco-friendly Goods and Services by the State and other entities (Law No. 100 of 2000). The conservation of resources and reducing waste is a necessity in Japan as a result of the constrained land area, constrained raw materials and less space for disposal. In fact, different laws dictate recycling in various sectors of society, including construction and demolition (C&D) waste materials. Remarkably, around 99% of the pavement that is removed is reused and recycled into new pavements [18]. Japan has accomplished this unprecedented level of RAP utilisation as a result of numerous decades of in-depth research and field performance evaluation. The practices and standards that have been developed have proved to be equally effective for high RAP mixes and virgin mixes.

2.2.4 China

In China, the usage of RAP has been encouraged in recent times as it has been locally accepted that its use can lower construction, maintenance and rehabilitation costs of asphalt pavement. However, it is difficult to indicate a specification that is used nationwide, however as per the Technical Specifications for Highway Asphalt Pavement (JTF F41-2008), 30% RAP seems to be the maximum content that can be used in mixes.

2.2.5 Europe

It is fairly normal in Europe to use RAP in dense-graded mixes and its use is regulated by the ordinance EN 13108-1:2006. This system is standardized in such a way that member countries are allowed to set agency-specific criteria within the framework provided in the standard.

2.2.5.1 Austria

In Austria, there is no exact limit on the percentage of RAP that can be used in mixtures. However, it is generally required that the aggregate properties of RAP comply with the constraints of the aggregates being used in the virgin asphalt material unless the RAP content is less than 10%. The softening point test results are utilised to assess the blend properties of RAP binder and virgin binder. However, the incorporation of RAP is not allowed in noise-reducing thin asphalt layers, open-graded asphalt (OGA) and SMA (Stone Mastic Asphalt).

2.2.5.2 France

The utilisation of RAP in unbound pavement layers is generally not a widespread practice in France. RAP content is usually kept below 30% when incorporated in granular base materials.

However, RAP is more commonly used inbound pavement layers for HMA, WMA, and cold in-place recycling.

2.2.5.3 Germany

According to the German standards, the utilisation of a high proportion of RAP is allowed in surface courses, contingent on the uniformity of the RAP material. There is no allowable limit as per literature, if RAP is incorporated into the surface layer, the aggregate properties of the RAP should comply with the normal constraints for surface layer aggregates. The highest allowable RAP in an asphalt mix is determined by the German asphalt specification, using the content of binder, softening point and proportional mass fractions of 0.063 mm, 0.063/2 mm and 2/maximum aggregate of the RAP material. As such, there are no specified RAP content limits for polymer modified mixes, as long as the properties of the blended binder, such as softening point, satisfy the criteria given for virgin binders. Lastly, the use of RAP in SMA and OGA is not permitted in Germany.

2.2.5.4 The Netherlands

In the Netherlands, high percentages of RAP are allowed in the different layers including the surface layer, there is no limit as per the specification provided that the RAP is of consistent quality and the final product complies with the normal specifications for dense-graded mixes. The use of RAP is not permitted in SMA and OGA, the latter of which is widely applied in the Netherlands.

2.2.5.5 United Kingdom (UK)

In the UK, 10% RAP in bituminous surface layers is allowed, but the RAP mixes have to comply with the same performance criteria as asphalt mixes containing only virgin materials. Ever since the UK adopted the EN framework of specifications, the specifications in the EN

13108-8:2005 standard series described above also apply to surface mixes containing RAP in the UK. The utilisation of up to 10% RAP in SMA mixes is allowed in the UK.

2.2.6 Australia

Current Australian practice only permits the utilisation of up to 30% of RAP in asphalt mixes [5]. Various state road agencies in Australia put requirements on the uniformity of the RAP material and the management of RAP stockpiles.

2.3 Characteristics of RAP

During the service period of HMA, the aggregates and especially the binders in the mixture undergo changes in this rheology and chemistry that would then need to be considered the mix design of new mixtures with RAP.

2.3.1 Properties of RAP Binder

The binder in RAP has undergone two separate phases of aging: short term ageing during construction and being subjected to air at temperatures reaching around 165^{o}C or higher; and long-term ageing primarily through the oxidative reactions between the bitumen and oxygen in the presence of air. This level of ageing is also influenced by the void content of the HMA as the binders retrieved from porous HMA have reported higher levels of ageing than regular HMA [19]. Studies have also reported that larger the deterioration of the pavement preceding the recycling, greater the differences in the characteristics of the binder. An example of this is the reduced oxidation sensitivity in pavements that are maintained better [20]. As a result of the changes in binder chemistry during ageing, RAP binders are considerably stiffer than virgin binders and exhibit different rheological characteristics. Hence, the blending of virgin and RAP binders to achieve desired properties is a significant design element in RAP mixtures. The properties of aged binders are also affected by the extent of moisture damage on pavements as the reuse of stripped HMA as RAP may increase the probability of reoccurrence in the new mixtures [21].

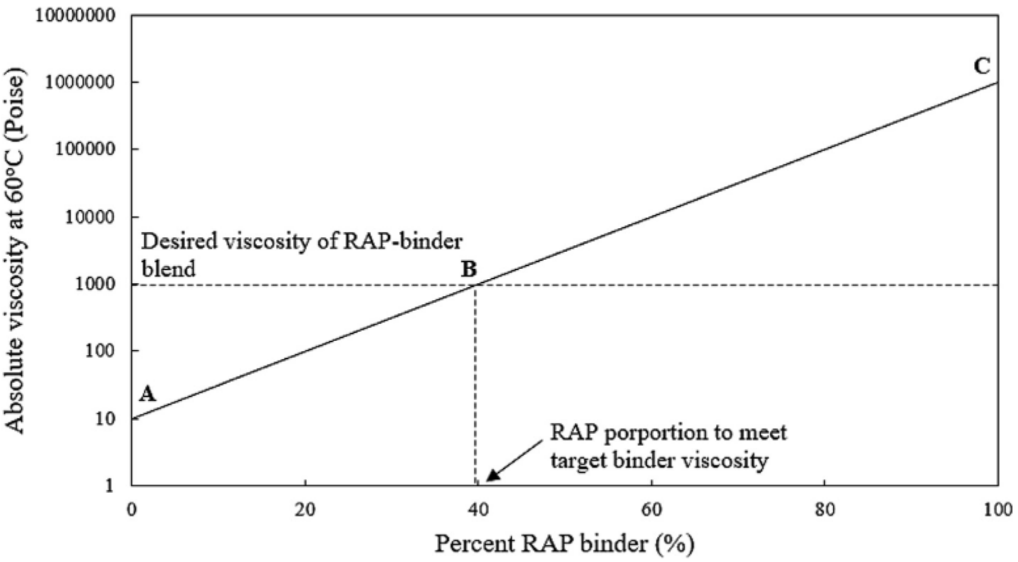
2.3.2 Rejuvenation of RAP Binder

To reduce the stiffness of aged binders, recycling agents such as rejuvenators are sometimes used to restore their rheological properties and soften it. These agents are expected to lessen the viscosity of the RAP binder and reinstate its original properties, in terms of rheology [22]. It is understood that binders lose some of its maltene components during ageing, hence the rejuvenating agents generally contain fractions to restore it to its original state. However, most commonly used rejuvenators are sold as proprietary materials which makes it difficult to suggest a universally applicable description. In general, rejuvenators are known to decrease the loss of surface fines and the formation of further cracks; however, they will also decrease pavement skid resistance for a short time. As a result, rejuvenators are generally suitable for roads that have low-volume and low- density. The selection of a rejuvenator depends on the stiffness and quantity of the binder in the aged pavement. Generally speaking, the lower viscosity rejuvenator types can be utilised to reinstate aged binders of elevated viscosity and vice versa. Based on these specifications, a recycling agent must have a low enough viscosity to mix with the RAP binder, and also have a high flash point for safety concerns. It is also necessary that the rejuvenator must not evaporate rapidly during the mixing and construction stage. As a rule of thumb, the ratio of binder viscosity at 60°C is exercised as a gauge of the rejuvenator's durability [22].

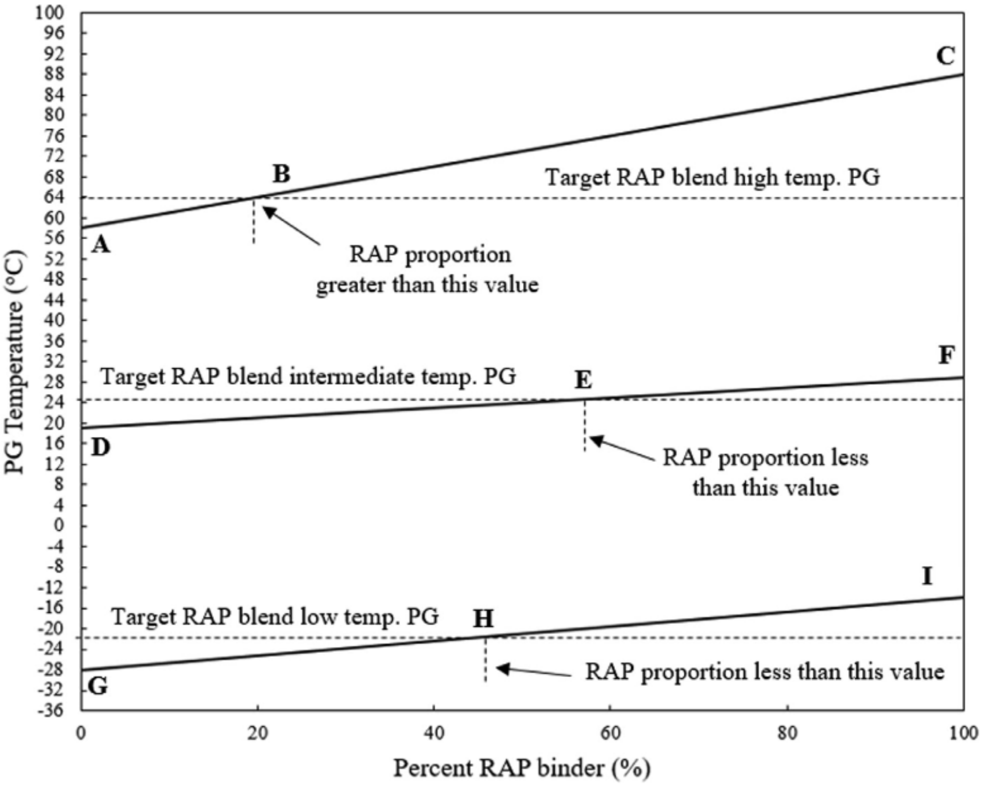
2.4 Mixture Design and Properties of RAP Mixtures

2.4.1 Selection of Binder Grade and RAP Proportion

The usage of RAP in new pavement mixtures introduces stiff binders into mixtures which often necessitates the change of virgin binder grade during mix design. Often times a softer grade is introduced into the mixture to ensure the combined blend meets target specifications. The earliest methods suggested a three-tier system to select the virgin binder [23]. As per the first tier, the grade of the fresh binder should not be altered if less than 15% of RAP is used. The second tier suggests if the proportion of RAP is between 15 and 25 %, then one performance grade can be lowered for the fresh binder. Lastly, if the proportion of RAP to be added is larger than 25%, the usage of blending charts is recommended. However, some studies have suggested that all tiers should use blending charts due to the variation in RAP source and properties [3]. Two methods have been reported for the creation of these charts, based on absolute viscosity and performance grading (PG) respectively [24]. The absolute viscosity method entails initially evaluating the absolute viscosity of RAP binder and fresh binder as per ASTM D2171.The absolute viscosity of the fresh binder at 60°C is plotted at point A as seen in Figure 2.1 (a), and the absolute viscosity of RAP binder at the same conditions is plotted at point C. These points are linked by a straight line and a corresponding parallel line is drawn through the target blend which intersects AC at point B. The vertical intercept at the x-axis estimates the proportion of RAP that can satisfy the viscosity of the blend. As per the PG method, the low, intermediate and high-temperature grades of the fresh and aged binder are firstly assessed. Figure 2.1(b) shows the typical graph wherein the high-temperature PG of the aged and fresh binder is plotted as point A and point C respectively. A and C are then joined by a straight line, and a parallel line is drawn via the required viscosity of blend, crossing the AC (viscosity line) at point B. The vertical intercept of the point at the x-axis estimates the content of the RAP proportion required. A similar procedure is repeated to establish the percentage of RAP required to satisfy the intermediate and low-temperature requirements. Alternatively, this procedure may be modified on the contrary case, i.e. if the proportion of RAP percentage to be incorporated is fixed. Hence, the PG of the virgin binder would need to be altered to meet the required specifications.



a) Absolute viscosity method



b) PG method

Figure 2.1 Commonly used blending charts, *adapted with permission from [25]*

2.4.2 Mix Design Procedure

Some of the other factors that need to be considered for the design of mixtures with RAP include the capacity of plants to heat aggregates and fulfill volumetric requirements. The technique for designing mixtures with RAP materials is comparable to normal mixtures, regarding the RAP aggregate as regular aggregate, however, the amount of binder in RAP material needs to be accounted for. This is done using solvent extraction or ignition tests. Nevertheless, there is known to be considerable inaccuracy when calculating this, which may lead to errors when determining volumetric calculations, as it is built on the effective asphalt binder content of RAP.

2.4.3 Properties of RAP Mixtures

The introduction of RAP creates mixtures that have distinct rheological properties as compared to 100 % virgin mixtures. This is principally as a result of the design constraints and complexity of introducing highly variable materials like RAP into mixtures.

2.4.3.1 Modulus

The impact of varying the percentages of RAP on the modulus of asphalt mixes have been examined by many previous works [26,27]. A previous study explored the properties of mixes containing different percentages (0, 20, 40 and 60%) of RAP. It was seen that the magnitude of the increase of the modulus depends on the softness of the fresh binder; the softer the fresh binder, the greater the relative rise in the modulus [26]. In another study, it was reported that hardened RAP binder causes a surge in the modulus of mixes with higher RAP content resulting in higher mix stiffness [27]. Varying RAP content (0, 15, 25 and 40%) also reported that using a higher RAP content generally enhanced the dynamic moduli of the mixes [28]. For those mixes where softer grade binders were used, the moduli of the mix were seen to be typically lower than original grade virgin binder mixes and these differences were also statistically significant.

2.4.3.2 Fatigue

A previous study indicated that an optimum fatigue performance of mixtures occurs at RAP percentages of 20% and 40%, and there is no significant disadvantage of incorporating RAP in mixes in terms of fatigue performances [26]. Similar results were obtained from other studies which included mixes with 0 to 30% RAP and showed it to improve fatigue performance [29]. However, contrary results have also been reported suggesting that the addition of RAP resulted in a declining tendency of performance related to fatigue in four-point bending tests, for mixtures comprising 0,20,40 and 60 % RAP. One study also demonstrated a decline of fatigue performance in mixtures with RAP content higher than 20%, when evaluated in contrast to the performance of mixes with only virgin materials [30]. This study also showed that some negative impacts of using RAP such as the brittle nature of the binder may be counteracted by using a softer fresh binder. Two methods for improving the fatigue resistance of mixes with RAP have been investigated [31]. One method was to use a greater quantity of fresh binder, and the other to lower its grade. A string of mixtures with different RAP contents of 0, 25 and 50% was designed and manufactured, and these mixes were tested to evaluate for surface and reflection cracking and rutting using standardized laboratory tests. Complementary to these mixes, two other types of mixes were manufactured with marginally higher binder contents than the optimum design binder contents and mixes that used a softer fresh binder. The results suggested that the quantity of fresh binder may be increased by 0.1% for every 10% of RAP binder in the mix for up to 30% RAP. However, for quantities higher than this, a softer grade binder should be employed to enhance crack resistance.

2.4.3.3 Rutting

The impact of incorporating RAP on the rutting performance of asphalt mixes is well reported and that the increased hardness of the binder blend results in the increase in rut resistance of mixes [3,29]. However, this may be most compliant with traditional mixes and not for SMA mixes. For SMA mixes, some literature has reported that the inclusion of RAP did not substantially impact rutting properties [32]. However, for SMA, this could largely be related to the influence of coarse aggregate interlocks and less to binder viscosity.

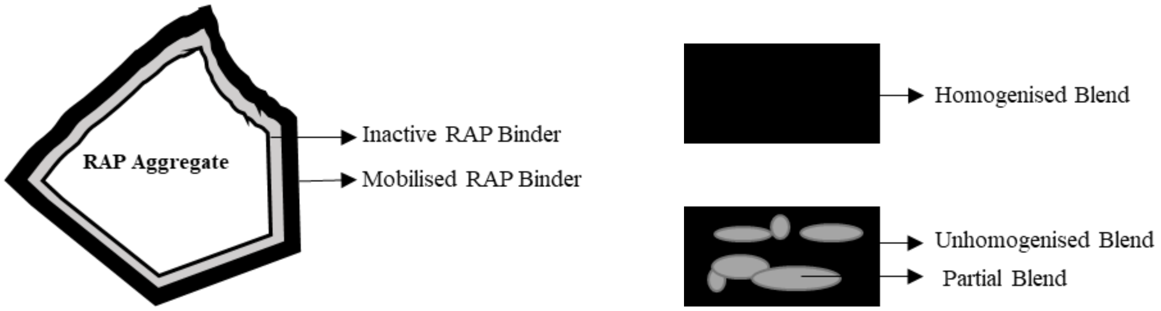
2.4.3.4 Moisture Susceptibility

Due to the brittle nature of aged binders, the moisture susceptibility of mixtures with RAP is a common concern for practitioners. In one study, mixes were prepared with varying RAP content from 15% to 30% and placed as a base and surface layer [33]. After placement, cores were taken from this pavement and also post two years in service. These samples were then evaluated by moisture susceptibility tests which showed that all the base and surface layer mixes passed the specifications even after two years in service. Further, the visual assessment of the cores found no excessive stripping. In another study, it was investigated whether there would be any apparent differences in performance between the newly introduced high RAP mixes and low RAP mixes that had already been in use [34]. The predisposition to moisture was assessed using the tensile strength ratio (TSR) tests and the findings suggested that the mean TSR values of mixes with RAP and control mixes were similar. One prominent study also investigated the performance of asphalt surfacing mixes with very high RAP contents of upto 50% [35]. Mixtures with 50% RAP showed acceptable resistance to moisture damage and thermal cracking. Satisfactory correlations were also detected among the measured critical temperature of recovered binders and expected ones from the blending chart. Previously in 2009, pavement sections with 50% RAP content were also built on a regional highway in Manitoba, Canada to assess the viability of using high RAP mixes in surface layers. This study mainly focused on the performance against moisture damage and thermal cracking and used both field produced mixes and lab produced mixes. The moisture susceptibility was assessed using the TSR test but with multiple freeze-thaw cycles instead of applying only one cycle. The results specified that all mixes met the minimum requirements i.e. TSR over 80% after one freeze-thaw cycle, and hence concluded that asphalt mixes with 50% RAP had acceptable resistance to moisture susceptibility in contrast to mixes without RAP or low RAP content (15%). Lastly, it has been reported that for SMA mixes, the TSR in moisture sensitivity tests increased with a higher content of RAP [32].

2.5 Mobilisation and Blending Phenomena

The significant variability in results reported above when incorporating RAP into mixtures is mainly due to the many unknowns in the mix design. One of the biggest apprehensions is regarding the extent of RAP binder mobilised and subsequently blended with the virgin binder during mixing. This area is the main focus of this dissertation and is a critical design variable that can significantly alter and affect mixture performance.

During mixing, the aged binder covering RAP aggregates is activated and becomes available to be mixed with the virgin binder. However, questions remain regarding various facets of this process. Firstly, what proportion or is all of the binder covering RAP aggregates available to be mixed with the virgin binder? Further, how well do the aged binders that are mobilised during mixing blend with the virgin binder? These extents of how these factors influence a mixture plays a significant role in the overall mixture performance. For example, if the mix design assumes all the binder covering RAP aggregates is available to be mixed with the virgin binder when some of it is unavailable to be mixed, this creates the potential for creating under-asphalted mixtures which can be easily prone to cracking and moisture damage. On the other end, over asphalted mixtures that can result from not considering the influence of the RAP binder will produce a mix stiffer than expected and an ensuing rich mix. Further, the extent of blending between these different binders will also affect the performance of mixes. The blending scenarios are presented in Figure 2.2. These issues are additionally confounded with the incorporation of recycling agents such as rejuvenators and warm mix additives (WMA).



a) Activated RAP Binder b) Blending Scenario

Figure 2.2 Mobilisation and Blending Phenomenon in RAP Mixtures

Most specifications assume that all the binder covering RAP aggregates are available to be mixed with the virgin binder [1]. Further, it is presumed that the RAP binder completely homogenises with the virgin binder to generate a homogenous mixture blend with target properties. According to this theory, the RAP binder achieves adequate workability during the mixing process to contribute and fully blend with the added virgin binder. Nevertheless, many research studies have indicated this may not be the exact case in practice [6,36]. There are primarily two opposite cases that have been considered: the mentioned complete availability of aged binder in RAP and the opposite black rock effect, which insinuates of a double coating of RAP binder and virgin binder. The black rock effect also implies that RAP aggregates merely behave as rocks and do not contribute any usable binder to the overall mix design [4]. However, it is now generally believed among practitioners that the aged binder does not behave as a black rock, and its full availability may also not be possible. A more realistic scenario is partial availability of aged binder in RAP wherein some percentage of RAP binder is active and mixes with the virgin binder [36]. Due to these uncertainties, many regulatory frameworks specify caution when defining targets for RAP mixing and blending [5].

Specifically, the extent of RAP binder mobilisation and blending of RAP mixtures have been studied by many researchers in the past using various rheological and chemical techniques [37].

Some researchers used the Hirsch model and other comparable methods to forecast mixture properties including dynamic modulus |E*| of blended binders extracted from mixtures, through matching their master curves measured under laboratory conditions [8,9]. Regarding the chemical methods, gel permeation chromatography (GPC) and Fourier transform infra-red (FTIR) spectroscopy have been the main tools used to assess the extent of blending and RAP mobilisation. Many research efforts have been undertaken using GPC which has consistently shown a nearly linear relationship between the percentage of LMS (large molecular size) and percentage of RAP mobilized [7]. FTIR, by comparison, has been utilised to a lesser extent but also proven to be effective in verifying the mobilisation and blending efficiency of recycled asphalt mixtures [38]. But in many of these previous studies, characterizing the extracted binder required the separation of RAP and virgin aggregate. Hence, a gap gradation or certain aggregate type was usually used. Overall, the results reported by these efforts have been largely variable as some studies have reported a high level of mobilisation and blending may be conceivable [39]. Conversely, studies have also indicated limited or partial mobilisation [36].

Several factors have been reported to influence the level of RAP binder mobilisation and the blending of binders in RAP mixtures. Increasing the temperature of mixing has been shown by several studies to be able to mobilise RAP binder by reducing its viscosity and making it more available to be mixed with the virgin binder [40,41]. Similarly, the duration of conditioning time has been shown to be proportional to the extent of blending between binders [42,43]. Raising the mixing time has also been revealed to increase the level of blending in RAP mixtures [44]. Few studies have also shown that if the RAP percentage is high, additional energy would be needed to mobilise the aged binder [45,46]. The use of additives such as WMA additives as recycling agents is also known to increase the blending of binders by softening the aged binder [36]. When virgin aggregates have high angularity, it has been reported that aged binders may be better mobilised as compared to more rounded aggregate

[39]. Lastly, some other factors such as the surface texture of virgin aggregates, aggregate absorption, mixture reheating, etc have shown to have an influence on this mobilisation and blending process [47,48]. Overall, there is considerable variability in the results available in the literature and there is limited understanding regarding the fundamental interaction mechanisms of the binders which may be contributed to these results.

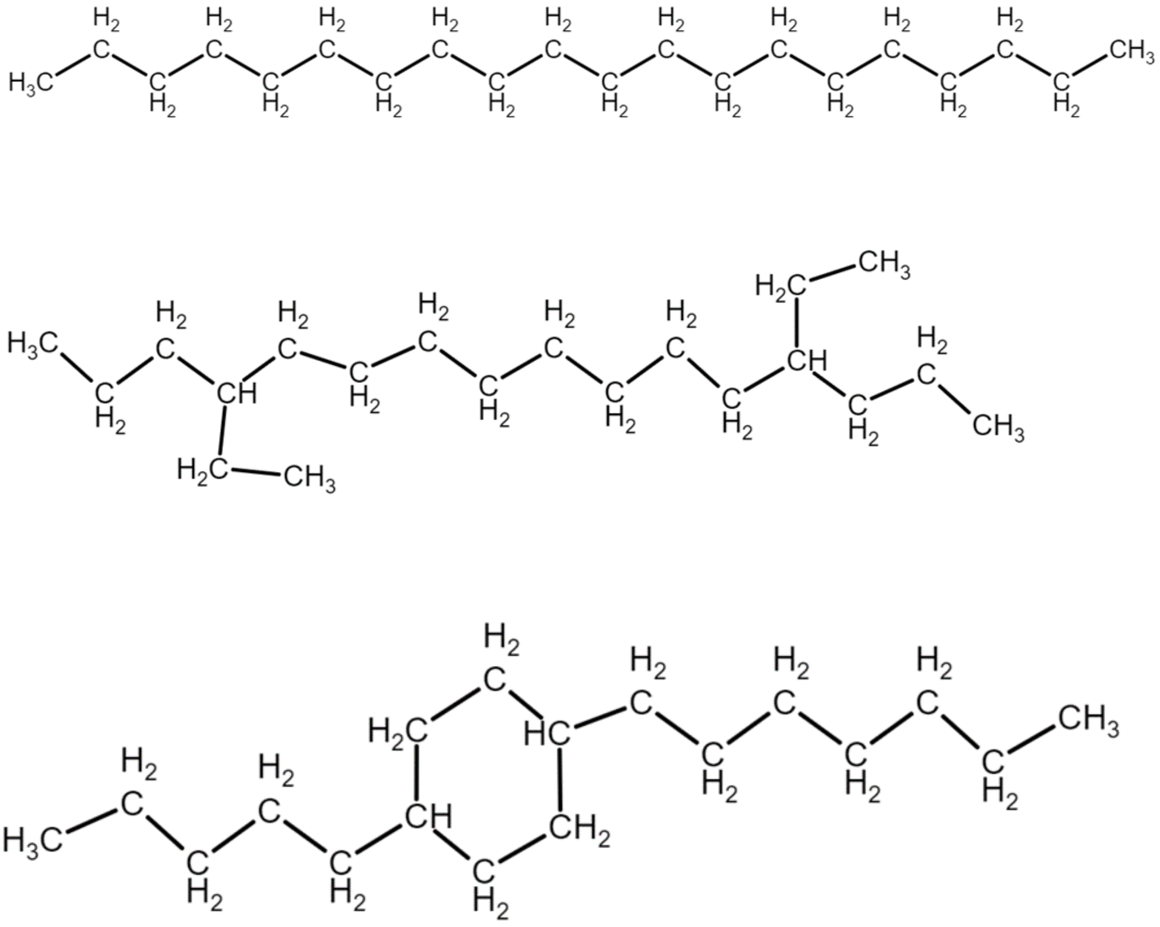
2.6 Chemistry of Binders

2.6.1 Bitumen

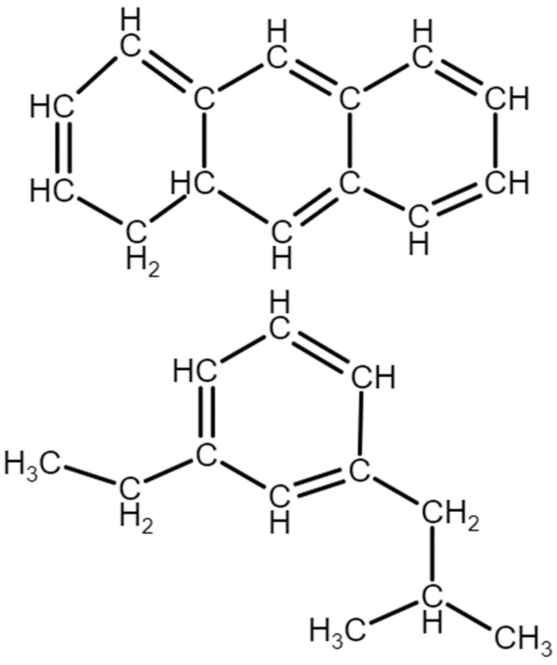
Bitumen is a complex material to study as it is composed of thousands of diverse hydrocarbon molecules and small quantities of heteroatoms like nitrogen, oxygen, sulphur and trace metals [49]. The various properties of bitumen such as binder grade could show large discrepancies, as a result of the different origins of crude oil and the production process such as distillation, cut-back temperature, storage conditions, etc. In terms of molecular structures, bitumen is a mixture of a variety of hydrocarbons: aliphatic, aromatic and a combination of both aliphatic and aromatic. The aliphatic molecules are saturated polycyclic structures, long-chain or branched paraffins or unsaturated olefins. The main constituents of the aromatics are the different polyaromatic structures with their fused rings. Moreover, various amalgamations of these structures are present with saturated hydrocarbon side chains and substitutions of heteroatoms like nitrogen, sulphur, and oxygen. These heteroatoms induce polarity in bitumen with nitrogen and oxygen being the main contributors to it. These atoms generate an inhomogeneous distribution of permanent dipoles and result in some polar interactions and hydrogen bonding. The molecular weight range of bitumen is quite varied ranging from 20-110 carbons and plays an essential role in its various physical properties [50]. The various molecular interactions in the bitumen are the dominant cause for the formation of structures within. The main interactions in bitumen are dispersive interactions, hydrogen bonding interactions, polar interactions, and π-π-interactions. Out of these dispersive interactions are understood to be the most dominant and have been linked to effect numerous properties of bitumen such as boiling point, viscosity, etc.

2.6.2 Solubility Fractions and Models of Bitumen Structure

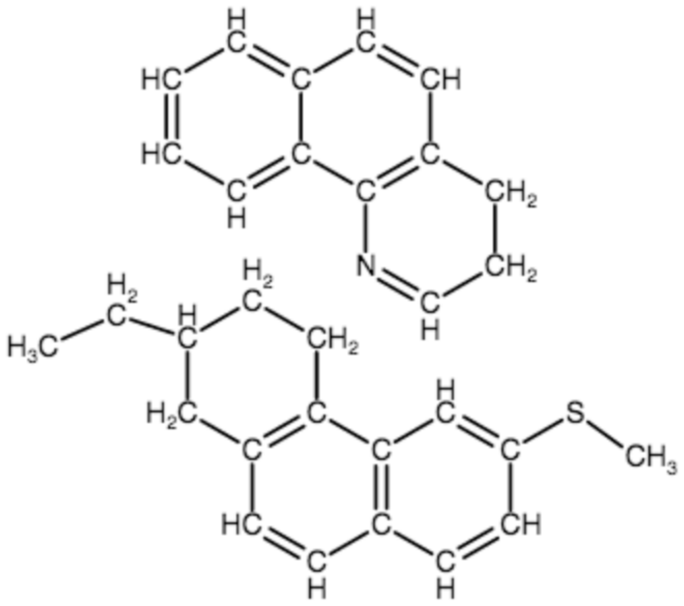
The detailed identification of individual bitumen molecules is evidently an unattainable task, however, groups of molecules exhibiting similar chemical behaviour can be grouped or correlated together to identify the building blocks and properties of bitumen. Firstly, the average chemical compositions and functional groups of bitumen were identified using different analytical techniques like mass spectroscopy and infrared spectroscopy (IR) [51]. In general, there is not known any relationship between the functional groups and physical properties, except for the carbonyl and sulphoxide groups which may be used for identifying the extent of oxidation. Various separation techniques based on different properties like molecular size, solubility, polarity, etc have also been introduced. The most frequently used practice is cantered on the partition of bitumen into its polar fractions based on the increasing polarity and polarizability, and referred to as saturates, aromatics, resins and asphaltenes (SARA) fractionation [52,53]. The probable chemical structure for each of these fractions is shown in Figure 2.3 [53]. Saturates, aromatics, resins are often clubbed together as referred to as maltenes as they can be separated from asphaltenes when dissolved in n-alkanes. Asphaltenes have weak molecular interactions with n-alkanes are known to be the building blocks of bitumen, and central to its rheological properties. However, it must be stated that these fractions are not discreet entities by any means but signify experimental limits of an incessant range of molecules, and hence their individual properties could differ even inside a fraction. These SARA fractions are hence composed of different molecular classes. Saturates are mainly composed of paraffins and naphthenes and aromatics are a mixture of paraffin, naphthenes, and aromatics with sulphur containing groups. Resins contain classes of molecules similar to aromatics with multi-ring structures and heteroatoms. Lastly, the asphaltene fraction consists of paraffins, napthenes, and aromatics in polycyclic structures with heteroatoms.



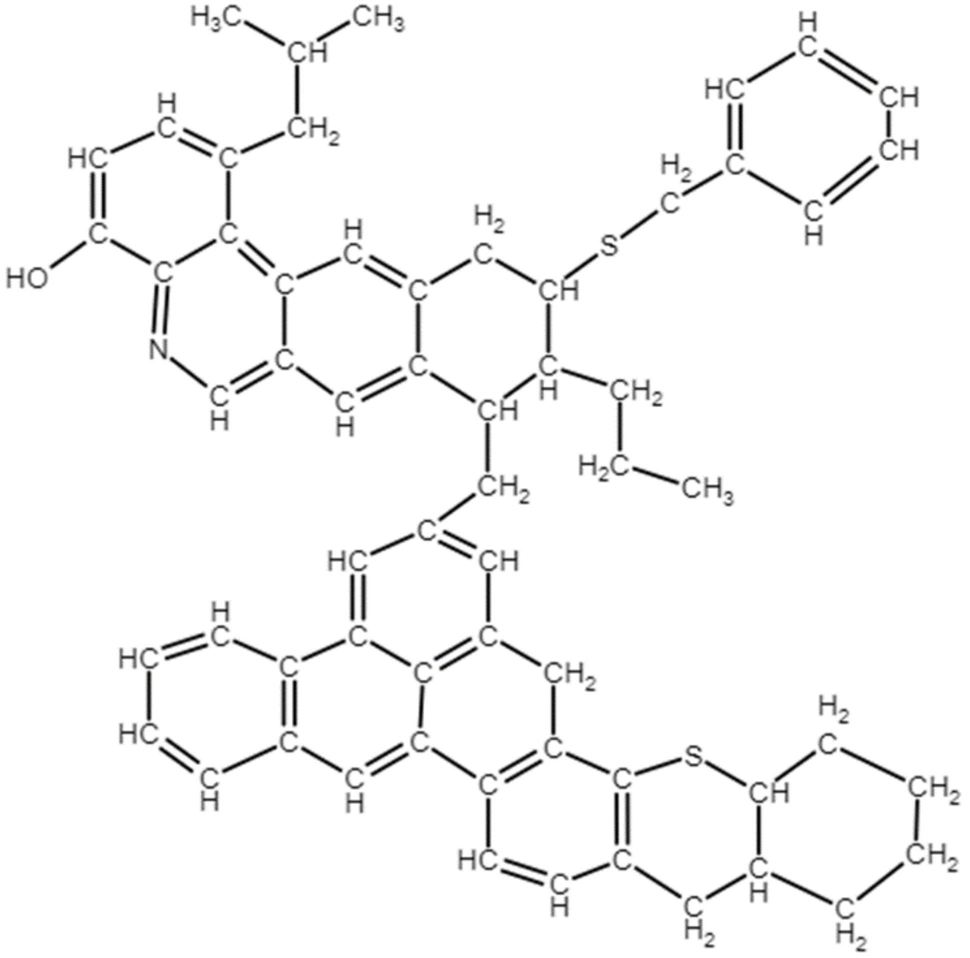
a) Saturates



b) Aromatics



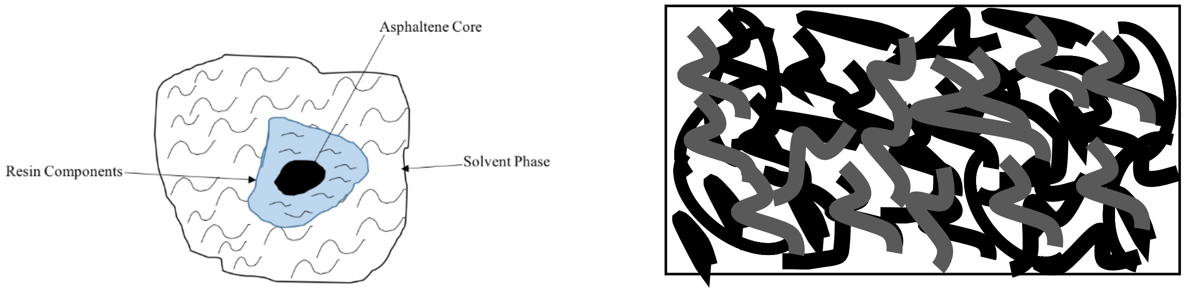
c) Resins



d) Asphaltenes

Figure 2.3 Molecular structures of bitumen fractions as per polarity-based separation

The precise microstructure of bitumen has been a prolonged topic of discussion for bitumen researchers and various models have been suggested by scientists to explain the structure and dispersion of various molecular fractions in it. The two most commonly used models are presented in Figure 2.4. The most widely used model is the colloidal model wherein bitumen is defined as a colloidal system in which asphaltenes of a higher molecular weight are dispersed in an oily medium of maltenes [54]. This model has been further developed into sol and gel structures, which explains the rheological behaviour with respect to the assumptions of each model. A sol bitumen consists of highly dispersed non-interacting micelles whereas a gel bitumen consists of organised asphaltenes with a network of agglomerated structures. In terms of its rheological properties sol bitumens generally, show a Newtonian behaviour whereas gel-like bitumen has predominantly non-Newtonian behaviour. In reality, most bitumens show properties of both sol and gel structures and transitional rheological properties [55,56]. Another model is a single-phase model, established through the Strategic Highway Research Program (SHRP) and commonly stated as the dispersed polar fluid model [57]. This model based on the polarity of molecules proposes that bitumen is composed of a mixture of various non-polar and polar molecules. The polar molecules are expected to associate by weak forces dispersed within the neutral portion of the material. This premise has been used to develop solubility-based models for bitumen which is based on mutual solubility of molecular fractions and discussed further in the next part of this chapter.



a) Colloidal Model

b) Dispersed fluid model

Figure 2.4 Models of bitumen microstructure [58]

2.6.3 Molecular Interactions

2.6.3.1 Dispersive Interactions

The dispersive interactions in bitumen can also be derived mathematically from electronic polarizability and refractivity using the equation [50]:

$$\alpha = \left(\frac{3}{4\pi N_A}\right)\left(\frac{M}{d}\right)\left(\frac{n^2-1}{n^2+2}\right) \qquad (2.1)$$

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 result of temporary dipoles, due to fluctuations of electrons around a molecule. Dispersive forces are generally considered to be a weak intermolecular interaction. However, it has been described to be a vital form of interaction between molecules in bitumen and impacts its physical properties.

2.6.3.2 Polar and Hydrogen Bonding

Polar and hydrogen bonding interactions are a result of a disproportion of the electron dissemination in molecules where covalent bonds are used to link atoms with dissimilar electronegativity. Strictly speaking, polar and hydrogen are generally stronger than dispersive interactions for small molecules. However, for larger hydrocarbons with lesser polar groups, dispersive interactions are more dominating. Studies have shown that the extent of polar molecules such as oxygen and nitrogen are relatively small in bitumen but may still affect its rheological properties [50]. Further, bitumen also contains sulphur based molecules, but its electronegativity is known to be very close to that of carbon and hydrogen, which are the building blocks of bitumen.

2.6.3.3 π-π-interactions

In bitumen molecules, π-π-interactions are anticipated to occur among delocalised π electrons [59]. The most common form of these interactions necessitates that one of the two molecules that interact should possess a robust electron-donating or attracting substituent which will allow for a tangible difference between clouds of electrons that overlap. For systems of aromatics that have four or more fused rings, this contribution is more pronounced. An example of this is when comparting the greater boiling point of polyaromatic hydrocarbons and saturated hydrocarbons. The π-π-interaction is enhanced when an aromatic ring is replaced with a more electronegative element such as nitrogen and oxygen [59].

2.6.4 Solubility Parameters for Bitumen

The physical properties of bitumen are determined by the extents of various interactions among its molecules. One of the methods used to evaluate the strength and characteristics of these interactions is to determine its solubility-based parameters. 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 [60,61]. 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 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 [62,63]. It was mathematically defined by:

$$\partial = \sqrt{\frac{\Delta H_V - RT}{V_m}} \qquad (2.2)$$

Where:

$\Delta H_V - RT$ = Heat of vaporization

V_m = Molar volume in the condensed phase.

In relation to this, Hildebrand solubility parameters have been shown to demonstrate the commencement of precipitation of asphaltenes and the interaction between asphaltene molecules. Most test procedures proposed in this regard used various ratios among solvents such as toluene and a precipitant like an n-alkane to predict the onset of precipitation. 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 these restrictions, 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) [63,64]. This approach describes an overall solubility parameter, δ_t (comparable of the Hildebrand solubility parameter), as:

$$\delta_t^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (2.3)$$

where the D, P, and H subscripts denote the extent of interactions from the dispersive, polar and hydrogen bonding parameters, respectively. 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 HSPs in three-dimensional space. This distance is commonly referred to as “Hansen Space”. However, determining the solubility parameters for a material like bitumen is a complex task as it includes a heterogeneous mixture of millions of molecules.

An approach that has been used previously consisted of the solubility testing with a large number of solvents with known solubility parameters. The assumption behind it was that a good solvent has a solubility parameter comparable to that of the solute while a poor solvent has a different solubility parameter, this allows for the assessment of the solubility parameter for the material in question i.e. bitumen. Using these, three-dimensional diagrams for the solubility sphere of bitumen can be drawn which entails its entire solubility in Hansen space. Figure 2.5 shows the solubility sphere of the bitumen fractions with three types of different interactions in the Hansen model. 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 are based on an approach termed as the “bitumen solubility model” (BISOM), introduced by Redelius (2000) [64]. 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 [65]. 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 [66]. Mutually soluble and compatible bitumens would theoretically have comparable relative solubilities in Hansen space and exhibit proportional strength of intermolecular forces such as dispersive force, hydrogen bonding and polar interactions. 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 its molecules [50].

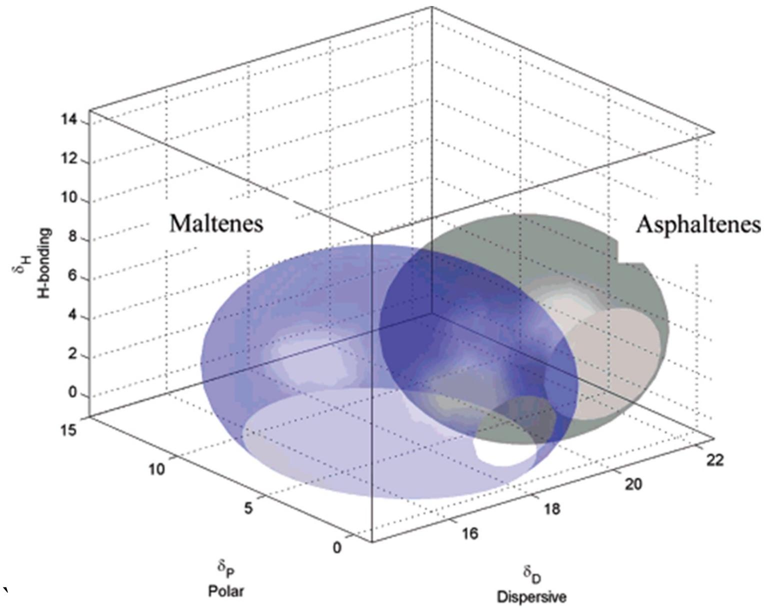


Figure 2.5 Hansen solubility model for bitumen fractions, *adapted with permission from [66]*

2.7 Microstructure of Binders

The microstructure of bitumen has been studied by various techniques. One of the earlier studies used phase-contrast and polarised light microscopy and predicted the two-phase properties of bitumen. Domains of few micrometers were observed and attributed to the saturate fraction [67]. Researchers have also some used techniques like confocal laser scanning microscopy and small-angle X-ray scattering [68-70]. The former reported the presence of ellipse-shaped features dispersed in the bitumen matrix. Although the use of such techniques has been reported, the most popular method to study the microstructure of bitumen has been through the use of atomic force microscopy (AFM) [71,72]. There exist thousands of scientific papers in literature which have employed the use of AFM to study the properties of bitumen, relating it to the various morphological features and rheology. AFM is most commonly used to study and characterise polymeric materials that show phase separation. Using AFM, the structural features of bitumen can be investigated at the length scale of nanometers to micrometers. Many studies have reported the existence of ellipse-shaped structures with height indentations and commonly referred to as “bee structures” as seen in Figure 2.6. The two-phase morphology can be seen wherein domain bee structures are dispersed in a continuous matrix phase. The chemistry and constitution of these structures have been a topic of research in many studies. Some studies have reported a larger number of bee-structures in binders with a higher asphaltene fraction [72]. It was also suggested that there was a disparity in stiffness along the rippled height of the bee-structure and could be comprised of more polar fractions such as asphaltenes and resins [73,74]. One popular finding was attributing the bee structures to the composition of the non-polar waxes present in bitumen. It was also shown that even after the removal of asphaltenes, the remainder of bitumen showed the characteristic microstructure. Researchers have also proposed a link between the microstructural structures and enthalpy peaks in differential scanning calorimetry (DSC) curves, leading to the assumption that the bee structures may relate to paraffin crystallization [75]. More recently, it has been concluded based on inter-laboratory tests that the interaction between crystallizing waxes and remaining non-wax chemical components in the matrix of the asphalt binder is the governing factor behind the appearance of the bee structures [76]. One of the other theories that have been reported is based on physical mechanisms unlike chemical compositions and is based on surface wrinkling theory [77]. It was suggested that the appearance of the bee structures could be caused by surface wrinkling as a result of the buckling of the bee laminate due to variations in phase stiffness with the continuous phase. However, so far there are no universally accepted conclusions on the origin of these structures and research efforts continue to identify the exact nature of these elusive entities. It is believed that the existence of such microstructures could have a distinct role in its physical and rheological properties of binders. To ascertain the correlation between the microstructure and morphology, many models and formulas have been used and upscaled to understand the different properties of materials. A testament to this is the multi-scale modelling approach that has become popular in recent times wherein bitumen, filler, and aggregates can be considered as microstructures in different length scales.

Nevertheless, no conclusive pieces of evidence have been achieved as of yet, which highlights the complexity of the bitumen material.

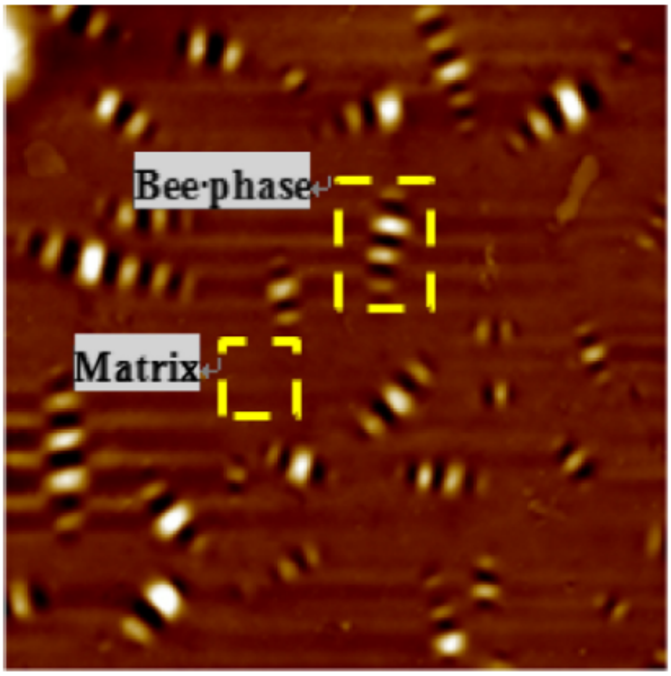


Figure 2.6 Bitumen microstructure image from AFM, *adapted with permission from [75]*

2.8 Bitumen Ageing

RAP binders are generally bitumens that have been through the normal service life of pavement. In this time, its rheological and physical properties are altered due to the ageing process which induces changes in the chemistry of its molecules. Chemical ageing is believed to be the aggregate of the oxidation reactions and polymerisation, and the evaporation of lighter components to a lesser extent [78]. Ageing results in the hardening of the material, which affects the rheological properties of RAP binders as discussed in section 2.3.1. The extent and vulnerability of a binder to undergo ageing naturally depend on inherent factors such as the crude source and manufacturing process. The ageing of bitumen is usually separated into two, short-term ageing and long-term ageing. Short term ageing refers to the ageing of binders in the course of mixing and laying of the mixture, conducted at elevated temperature whereas long term ageing implies to the oxidation of binders during the service life of the pavement. Short term ageing for binders are replicated by the rolling thin film oven test (RTFOT) and has been demonstrated to increase its viscosity and content of asphaltene by 1-4% [79]. Long term ageing, on the other hand, occurs for a lengthier duration of time and its extent depends on the position of bitumen within the pavement. Top layers of pavement are naturally more exposed to the environment as compared to lower layers. Other factors also contribute to the extent of ageing such as mix formulation, local climate bitumen thickness, etc. Hence, it is difficult to correctly describe and model in-field ageing. A pressurized ageing vessel (PAV) test is commonly used by practitioners to mimic the long-term ageing of binders. Nevertheless, it has been reported to only replicate the ageing level of up to 10 years or less [54]. The service life of pavements can normally extend from anywhere between 5-25 years. Volatilization also contributes to the overall ageing of binders, and is the evaporation of the lighter fractions and is considered a function of temperature. This is mainly a factor in the short-term ageing during production but has minor effects throughout the service life as well. It has been reported lighter oils remaining in the bitumen after the refining process are the primary fractions of volatiles that exist during the mixing process. When crude oil is distilled in a refining process, heavy fractions are split from the lighter fractions. Although lighter oils advance to the apex of the distillation column and heavy fractions to the base, they are never detached fully. Therefore, the amount these lighter fractions remaining in bitumen is variable and dependent on these.

2.8.1 Effect on Chemistry and Rheology

In terms of the SARA fractions, it is observed that the asphaltenes and resin fractions increase whereas the aromatic content decreases. It is widely regarded that aromatics generate resins which in turn generate asphaltenes [80,81]. However, saturates remain unaffected due to their low chemical reactivity. Interestingly, the asphaltenes produced upon aging could be dissimilar from the original due to various polymerisation reactions [82]. Some detailed studies have been directed regarding bitumen oxidation, which indicated a surge in asphaltenes molecular weight. In addition, H/C, N/C, and S/C ratio were reported to be deteriorating while the O/C ratio increased, which signals that the oxygen uptake of the asphaltenes was emerging corresponding with the release of sulphur and nitrogen [83]. In relation, the rate of asphaltene production has been shown to be fairly linear with time in both laboratory as well as field experiments [79,81]. Ultra-violet (UV) light is also responsible for the increase in oxidation by activating photo-oxidation reactions [84,85]. Such reactions generate polymerisation of asphaltenes, as well as for the lower fractions such as saturates. It is vital to notice that photooxidation is strongly radiation intensity-dependent as opposed to thermal ageing which is primarily temperature-dependent. Ageing has been a topic of widespread research as it significantly impacts the rheological behaviour of binders. In fact, it can be regarded as the most significant factor that influences the deterioration of properties and the termination of the service life of pavement through cracking issues as discussed as 2.4.3. Viscosity is frequently utilised as a gauge for determining the extent of ageing, wherein an ageing index is defined as the viscosity ratio or as the comparative increase in viscosity versus time [84]. Previous studies have observed that room temperature viscosity increased linearly versus aging time for a time period of up to 15 hours [78]. It has also been described that various types of bitumen show dissimilar kinds of kinetics at high and low temperatures [86].

2.9 Blending of Bitumens

The blending of different bitumens is a common practice to achieve the desired final grade of binder [49]. In the simplest sense, the mixing of aged binder in RAP with virgin binders is a comparable process; although the influence of aggregates and mixing conditions makes it a far more complicated in reality. The current understanding and specifications relating to this are quite similar to that blending of different bitumens, which is often practiced during manufacturing. Generally, it is believed that the mixing of bitumens of different penetrations gives a combined bitumen of somewhere close to intermediate penetration. This is useful as a rule of thumb for practitioners although there many exceptions to this rule especially when considering the mixing of bitumens with very different compositions such as aged binder and unaged binder. An example of this is the difference observed when bitumens of similar penetration were mixed together and resulted in a penetration maximum. For illustration, the mixing of 65% of one bitumen with penetration of 20 with another bitumen of the similar penetration resulted in a vastly different penetration of 42 [87]. Another indication of this phenomenon is the reported literature regarding the variability in properties of cross blended asphalt binders [88]. Viscosities of asphalt mixtures of blends have shown irregularities when compared with the viscosities of the original asphalt binders. The exact chemistry behind this is still not well understood and it is believed to be a result of an unequal combination of glass transition temperature and asphaltene content. RAP binders are known to contain higher asphaltene contents than virgin binders as a result of the transition of non-polar molecules to more oxygen comprising polar groups. Understanding the fundamental properties of this blending and its response to various pavement stresses is an imperative stage in the selection criterion of both virgin and RAP binders. However, there is little literature available in this regard.

2.10 Summary

The use of RAP is new pavement mixtures has been widely promoted by transport agencies around the world. Such technologies have been shown to potentially improve the sustainability of pavement and also provide comparable pavement performance as 100% virgin mixes. The following findings are summarized from the reviewed literature:

- Many transport agencies around the world allow for RAP content of up to 50% in new pavement mixes. However, on average most mixes have RAP content around 15-20% and rarely go above it.

- RAP binders have generally undergone both short term and long term ageing, which results in considerable changes in its original rheology and chemistry. Hence the distinctive characteristic of RAP binder is its high stiffness as compared to normally used virgin binders.
- The full availability of the binder present in RAP is generally deemed in the design of mixes. Mixes with a higher quantity of RAP (>20%) usually employ the use of blending charts or other similar methods. The accuracy of these charts to correctly predict the mixing phenomena is debatable.
- There is significant inconsistency when it comes to reported literature regarding the performance of mixes with RAP. In general, RAP mixes can deliver satisfactory results when it comes to rutting performance. However, the introduction of RAP may present problems in relation to moisture susceptibility and fatigue cracking.
- The significant variability in results reported when incorporating RAP into mixtures is mainly due to the many unknowns in the mix design. One of the biggest apprehensions is regarding the extent of RAP mobilised and subsequently blended with the virgin binder during mixing. There is inadequate understanding regarding the various facets involved in this phenomenon.
- The unique chemistry of bitumen gives its distinctive microstructural and chemical properties. Ageing, due to the natural oxidation of bitumen over time considerably alters the chemistry of binders.
- Blending of bitumens with different compositions to achieve target grades, such as aged binders with unaged binders is an intricate process. A fundamental understanding regarding the interaction mechanism between aged and unaged binders is deficient.

CHAPTER 3

EVALUATION OF RAP BINDER MOBILISATION AND BLENDING EFFICIENCY

The uncertain degree of RAP binder mobilisation has a substantial impact on the overall performance of RAP mixtures. In this chapter, a novel method to quantify the degree of RAP binder mobilisation and subsequent blending efficiency of RAP mixtures by utilising attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy as an assessment tool was proposed. Binders were recovered from laboratory bituminous mixtures with different percentages of RAP, prepared under different mixing conditions using glass-based aggregates as tracers. Parameters for assessing the relevant properties were then developed and validated through the means of dynamic shear rheometer (DSR) and gel permeation chromatography (GPC) tests.

Portions of the results and discussion presented in this chapter have been previously published in "Evaluation of RAP binder mobilisation and blending efficiency in bituminous mixtures: An approach using ATR-FTIR and artificial aggregate, Construction and Building Materials 179 (2018), 245-253"

3.1 Experimental Mix Design and Materials

The Marshall mix design was used to prepare the mixtures in this study. The virgin binder used was of penetration grade 60/70 (PEN 60/70) which is a common type of bitumen used locally. The specific gradation of the mixture is presented in Table 3.1. The coarse aggregates (greater than 5mm) and fine aggregates (smaller than 5mm) were local granite rocks. The RAP used was obtained locally from wearing course milling. The RAP binder was extracted as per AASHTO T164 and analysed through Saturate, Aromatic, Resin and Asphaltene (SARA) fractionation as represented in Table 3.2. The SARA fractionation was conducted as per ASTM D2007. The softening point and penetration tests were conducted as per ASTM D5 and ASTM

D36, and the obtained values are presented in Table 3.3. A mechanical mixer was used to mix all the samples for a period of 2 min to reduce variability and discrepancies between samples with regards to preparation [89]. As RAP contains aged binder, the mixtures prepared in this study were designed with consideration of the total contribution of the recycled binder. The binder content of the RAP was determined as per AASHTO T308 and found to be to 5%. For all the mixtures with 0%, 15%, 30% and 50% RAP materials, a total binder content of 5% were chosen.

Table 3.1 Mixture Composition

	Mixture Gradation	RAP gradation
Sieve Size (mm)	Pass ratio (%)	
14	100	100
10	85.0	94.1
5	58.0	87.8
2.36	38.0	70.0
1.18	26.0	50.2
0.6	17.9	32.7
0.3	11.0	19.2
0.15	3.4	9.7
0.075	3.0	3.4

Table 3.2 SARA Fraction of RAP

RAP	Composition (%)
Asphaltene	15.80
Saturate	24.23
Aromatics	19.53
Resin	40.45

Table 3.3 Softening Point and Penetration of RAP

Softening Point (^oC)	Penetration (0.1mm)
75.5	29

3.2 Glass Beads as Artificial Aggregate

As the primary objective of this study is to examine the amount of RAP binder mobilisation, the blend of mobilised RAP binder and virgin binder coating the fresh aggregates is of specific interest. In a real blending scenario, it is visually impossible to distinguish between RAP aggregate and virgin aggregates after mixing. Thus, in this study artificial aggregates in the form of borosilicate glass beads were employed. Beads of diameter 12 mm, 10 mm and 7.5 mm were used to make up approximately a 2% fraction of the overall gradation of the mixes by weight by adjusting the original fresh aggregates. Such a small fraction was chosen so that the effect of the glass beads in the mixing process and aggregate interaction would be negligible. The chemical composition and the proportion of glass beads used are shown in Table 3.4 and Table 3.5, respectively. Figure 3.1 shows illustrative images of the glass beads and glass beads dry blended with RAP. Prior studies have successfully used similar types of glass beads to characterise the mobilisation of RAP binder to virgin aggregates [90]. The consistent dimensions of glass beads make them useful for such studies. However, it does have the drawback of its relatively smooth surface as compared to the naturally rough surface of normal aggregates. To minimise this, the glass beads were initially blended with fresh aggregates to roughen the surface.

Table 3.4 Chemical Composition of Glass Beads

Chemical Composition	SiO_2-82% B_2O_3-12.4% Na_2O-3% Sb_2O_3/As_2O_3 - <0.01%
Density	2230 Kg/m^3
Melting Point	1500°C

Table 3.5 Weight of Glass Beads Used in Each Mixture

Glass Bead Types (*Number)	Weight (in gms)
12mm (*2)	7.17
10mm (*4)	8.88
7.5mm (*6)	7.08
Sum	23.13

a) Original glass beads b) Glass beads after dry blending with RAP

Figure 3.1 Pictures of the glass beads used

3.3 ATR-FTIR to Evaluate RAP Binder Mobilisation and Blending

Previously, chemical methods such as GPC and FTIR have been used to characterise oxidative ageing and its significance on the chemical composition of bituminous binders. FTIR is particularly interesting for researchers and engineers because of its accuracy and ease of use. Also, it does not require a large or controlled lab space in comparison to GPC. There is a prospect that with advancing FTIR research, parameters for mix design and optimisation could be derived from the FTIR results of bituminous binders. FTIR using attenuated total reflectance (ATR) is generally the most preferred method of characterisation as it offers faster sampling with limited preparation and also excellent sample-to-sample reproducibility.

3.3.1 Mechanism of ATR-FTIR

In ATR, evanescent light located in the region of contact between the sample specimen and a crystal of high refractive index is attenuated as a result of molecular vibrations [91]. The non-prism of the ATR-FTIR has an oblong and trapezoidal structure to allow several internal reflections which enhances the absorption spectra. The principle of ATR-FTIR is shown in Figure 3.2 [92]. Some of the major advantages of this method, especially when considering a material like bitumen is that the whole spectrum can be attained without solvent blankout and the chemical influence of the solvent can be averted. The crystal of the ATR consists of a transparent IR material with a high refractive index. The infrared beam generally enters the

ATR crystal at an angle of around 45°C and is reflected at the crystal to the sample surface. The light tends to not be directly reflected at the boundary surface but by a virtual layer within the optically less dense samples, termed to as the Goos-Hänchen effect [92]. The portion of the light wave that extends to the sample is termed as the evanescent wave. The intensity of the penetration is reliant on the wavelength, the refractive indices of ATR crystal and sample, and the angle of the entering light beam. Typically, it is in the magnitude of a few microns, and in the spectral regions where the specimen absorbs energy, the evanescent wave will be attenuated. The IR beam is then directed to the detector after one more internal reflection. In order to attain a high-quality spectrum, it is paramount that good contact is achieved between the sample and the ATR crystal as the light only penetrates the samples up to a few microns. In addition, the sample being tested must have a lower refractive index than the ATR crystal. In this study, a diamond ATR module with a refractive index 2.4 was used, which has been shown to be a suitable crystal for studying bituminous binders [93]. An image of a standard Bruker FTIR spectrometer is also shown in Figure 3.3

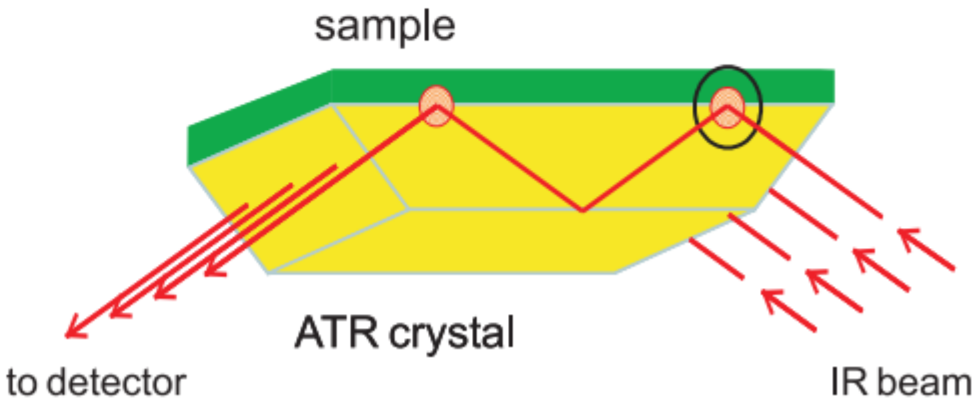


Figure 3.2 Principle of ATR-FTIR, *adapted from [92]*

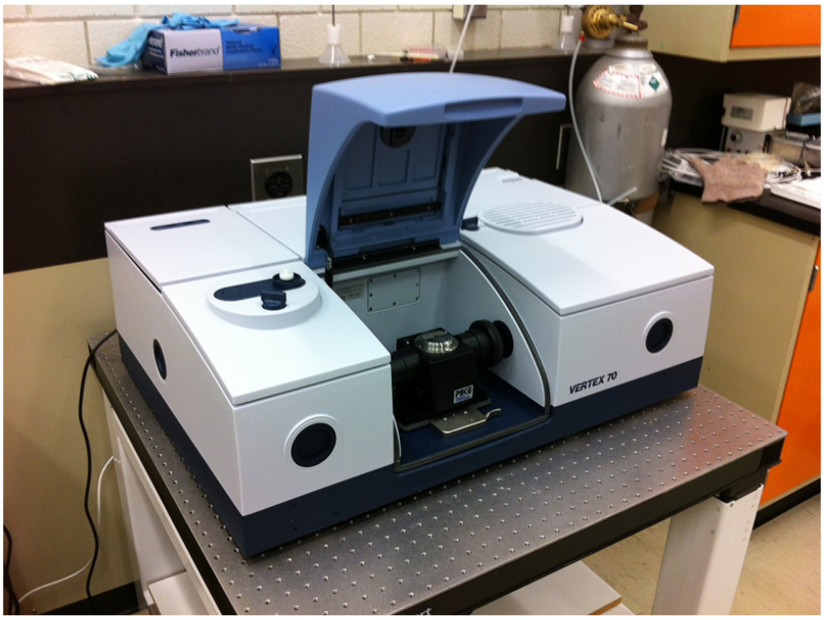


Figure 3.3 Bruker attenuated total reflection FTIR spectrometer

3.3.2 Application to Bitumen

The study of the natural oxidative ageing exposed by bituminous binders has been the prime focus of attention for asphalt researchers using FTIR. The variations in this level of oxidation have been used to correlate changes in the rheological and chemical properties of mixes in the past [6,38]. For the analysis of the obtained FTIR spectra of bituminous binders, many different approaches can be used. The spectra can be examined in its original form or be normalised prior to analysis. Unique values from absorbance bands may be used or a variety of wavenumbers could be considered by integrating the area underneath an absorbance spectrum in between a defined wave number. Lastly, the foundation for finding the area can be either using a tangential or an absolute baseline. One previous study used a statistical approach to study the repeatability and sensitivity of various FTIR analysis methods [94]. From the conclusions, it was advocated to work with a normalised spectrum, utilise an absolute baseline and integration of areas in favour of other approaches as it offers the most consistent results with regard to sample repeatability and sensitivity. As it is the most comprehensive work in recent times regarding FTIR analysis of asphalt binders, this study also employs the use of those recommendations as the basis of its analysis approach.

In asphalt binder chemistry, the carbonyl band (C=O) exhibited at around 1700 cm^{-1} and the sulphoxide band (S=O) exhibited around 1000 cm^{-1} of a bitumen spectrum are the major functional groups used to gauge the level of oxidation. However, the carbonyl band has been more commonly used and known to better correlate the level of long term ageing [6]. Binders extracted from RAP materials exhibit significantly higher levels of C=O bonds due to the natural oxidation of asphalt binder during the producing process and service period on pavement whereas virgin binders exhibit little or no C=O bond at this wavelength. This difference in oxidation can be utilised to approximate the amount of RAP mobilisation and blending in mixtures [38]. Figure 3.4 shows the FTIR spectrum of the RAP binder and the virgin binder, which shows the clear oxidation peak at the wavelength of around 1700 cm^{-1} for the RAP binder. Also indicated in Figure 3.4 is the analysis area of the FTIR spectra.

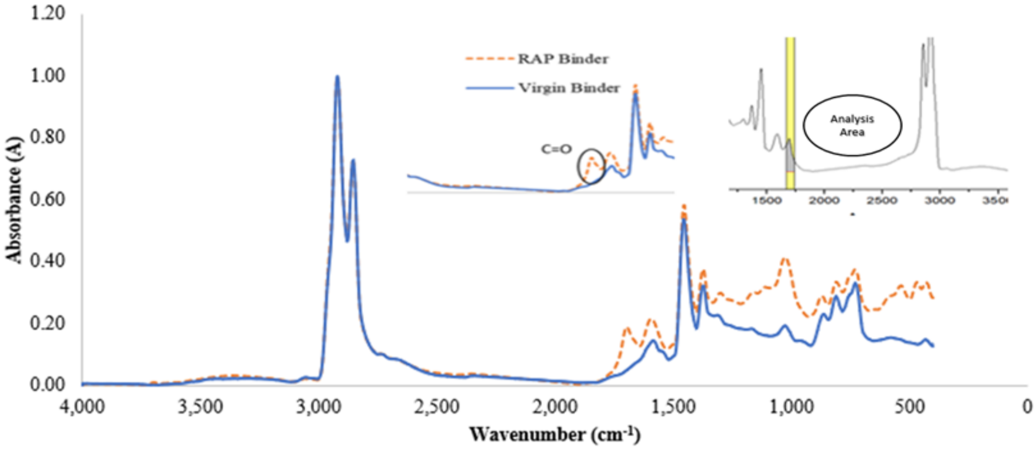


Figure 3.4 FTIR spectra of the virgin binder and RAP binder

The analysis approach of the various FTIR spectra involved the integration of areas, normalised spectra, and absolute baseline. Hence, the parameter for one spectrum can be defined as

$$\mathrm{IA}=\int_{w_{l,oa}}^{w_{u,oa}} VA_{norm}(w)\, dw \qquad (3.1)$$

where IA is the normalised integrated area using an absolute baseline at an absorbance value of 0; $w_{u,oa}$ 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 lower and upper wavenumbers for the carbonyl structural group was defined from 1666 to 1746 cm^{-1} [94]. The detailed analysis approach is further described in the appendices, section A.1.

Using Equation (1) as the basis, the parameters for characterising RAP mobilisation and blending efficiency were established. The binder recovered from the glass beads is expected to have a considerable amount of RAP binder mobilised as a result of the mixing process. In this study, a concept that the RAP binder is considered at 100% RAP character whereas virgin binder has 0% of RAP character was used. Based on this, a parameter to estimate the percentage of RAP binder in the recovered binders was developed. This parameter is used to represent the RAP mobilisation and can be described as follows:

$$\text{Percentage of RAP Binder Recovered (\%)} = \frac{IA_{BS}-IA_{VB}}{IA_{RAP}-IA_{VB}}*100 \qquad (3.2)$$

where,

IA_{BS} is the IA of the recovered binder from the respective sample;

IA_{VB} is the IA of the virgin binder;

IA_{RAP} is the IA of the RAP binder.

The term “blending efficiency” has been defined differently in many studies, and it has been previously used to describe various types of RAP binder mobilisation through the development of special parameters [38,95]. In this study, the idea of using artificially blended RAP binder and virgin binder to create an efficiency baseline was used. For example, when RAP binder and virgin binder are artificially mixed in the laboratory and then used to prepare asphalt mixtures, it is reasonable to conclude that the asphalt mixture with such kind of blended binder has full blending efficiency, whereas the asphalt mixture prepared with RAP, fresh aggregates and binder can be considered to have a blending efficiency of less than 100%. The FTIR index i.e. the IA produced from the binders with full blending efficiency can be employed to create the baseline for calculating the blending efficiency of the binders in the asphalt mixtures with RAP materials assuming homogeneity of mixing [96].

$$\text{Average Blending Efficiency (\%)} = \frac{IA_{BS}-IA_{VB}}{IA_{AB-i}-IA_{VB}}*100 \qquad (3.3)$$

where

IA_{AB-i} is the IA of the artificially blended binders; and i is the percentage of RAP binder.

993.4 Experimental Procedure and Methods

The results of the proposed parameters from the FTIR tests were validated through rheological and chemical evaluation using Dynamic Shear Rheometer (DSR) and GPC tests, respectively. Control mixtures with 15%, 30% and 50% RAP percentages were prepared at the temperatures of 135°C and 165°C as illustrated in Table 3.6. Regarding the mixing process, the glass beads were heated with the virgin aggregates at approximately 10°C higher than the sample mixing temperature before adding the pre-heated RAP [89]. Three replicates for each type of sample were prepared. Lastly, artificially blended binders with 15%, 30% and 50% RAP binder to virgin binder content referred to as AB-15, AB-30 and AB-50 in this study were also prepared. After mixing, the glass beads were collected as shown in Figure 3.5 and the binder was recovered using Trichloroethylene (TCE) solvent. Minimal temperature was used in the extraction process to negate any additional aging effects. The recovered binders were characterized through ATR-FTIR analysis 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. 3 samples were analysed for each mixture. Following each test, the optics were thoroughly cleaned using solvent and acetone. The DSR tests were conducted using an Anton Paar DSR machine as shown in Figure 3.6. The tests were conducted at the frequency range of 0 to 30 Hz at 30^{o}C. The GPC studies of the recovered binder samples were tested using a Shimadzu Prominence GPC system using two styragel columns as illustrated in Figure 3.7. GPC is based on size exclusion and molecules are separated on the basis of size. When a material with a combination of different molecules such as bitumen (dissolved in solvent) is applied to the top of the column, the smaller molecules are dispersed through a greater volume of gel than is accessible to the large molecules. Hence, the large molecules move more swiftly through the column and the mixture can be fractionated into different components as shown in Figure 3.8. These components are usually clubbed into different size ranges based on a distinct series of sizes, such as large molecular sizes (LMS), small molecular size (SMS) and medium molecular size (MMS). Importantly, a nearly linear relationship exists between the percentage of LMS (large molecular size) and the percentage of RAP mobilised [7]. Tetrahydrofuran (THF) was used to dissolve the binders to the required concentration and subsequently filtered through a 0.2 μm filter for testing. Subsequently, the large molecular size (LMS) percentages were calculated for the recovered binder as follows [97,98]:

$$\text{LMS\%} = \frac{\text{Area of first}\,\frac{5}{13}\,of\ chromatogram}{\text{Toal Area below the chromatogram}} * 100 \qquad (3.4)$$

The detailed analysis approach is further described in the appendices, section A.2.

Table 3.6 Control Samples Prepared

Temperature	RAP Content	Legend
135°C	15% RAP	15% RAP-135
	30% RAP	30% RAP-135
	50% RAP	50% RAP-135
165°C	15% RAP	15% RAP-165
	30% RAP	30% RAP-165
	50% RAP	50% RAP-165

Figure 3.5 Glass beads recovered after mixing

Figure 3.6 Dynamic shear rheometer (DSR)

Figure 3.7 Gel permeation chromatography system

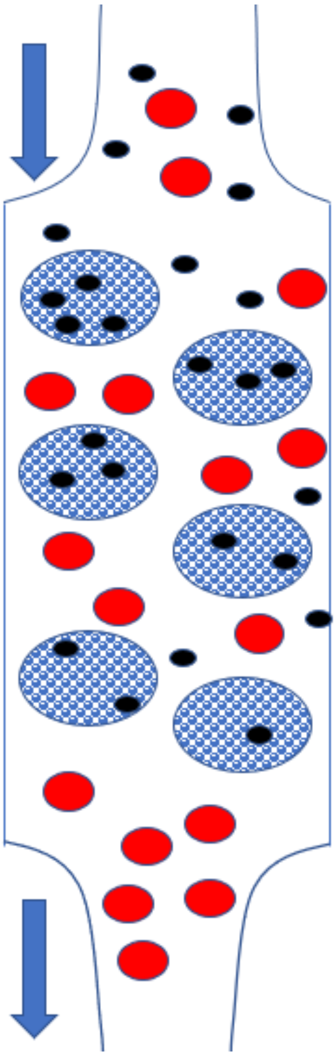


Figure 3.8 Principle of size exclusion in GPC [99]

3.5 Results and Discussion

3.5.1 Temperature Effect on RAP Mobilisation and Blending Efficiency

Initially, the recovered binders from the control samples were analysed using Eq (3.2) and the results are represented in Figure 3.9. It was observed that at all percentages of RAP added, there was significantly more RAP mobilised at a higher temperature than at a lower temperature. The mixtures prepared at 165°C showed on average close to 30% higher RAP mobilisation than mixtures prepared at 135°C. The results obtained are in accordance with other reported studies in which it was ascertained that in a mixing process, the RAP mobilisation is highly conditional on temperature [95,97]. The increase in mobilisation with temperature was more obvious at a higher RAP content as compared to a lower RAP content. It is likely that the additional availability of RAP aggregates may promote added interaction and mobilisation of RAP binder with the increase in temperature during the mixing process.

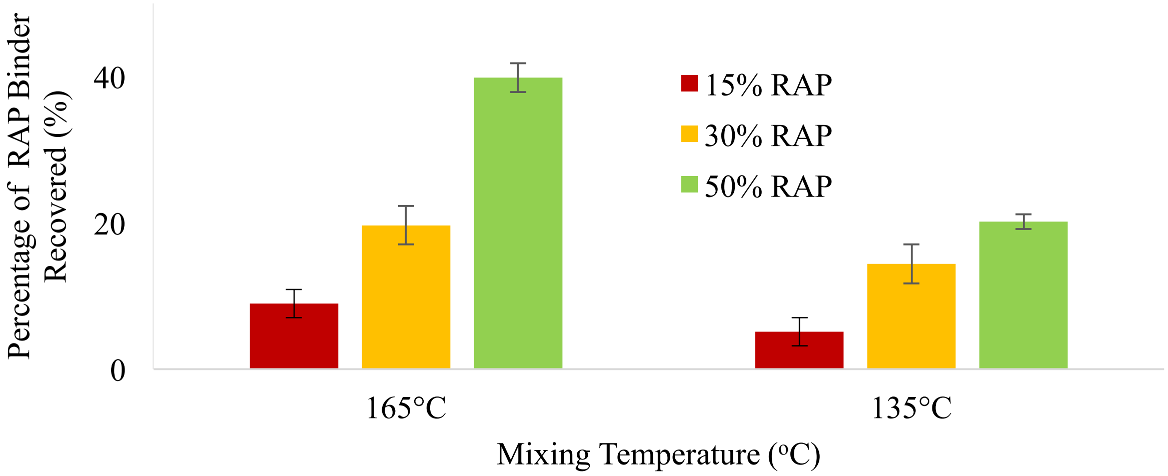


Figure 3.9 Percentage of RAP binder recovered for control samples

The blending efficiency was calculated using Eq (3) and represented in Figure 3.10. It was observed that the samples mixed at the temperatures of 165°C showed a higher efficiency of blending as compared to the samples mixed at 135°C. The samples with 50% RAP showed the highest average efficiency of blending as compared to the samples with 15% and 30% RAP contents. Approximately, the blending efficiencies ranged from 50% to 60% for the samples prepared at 165°C and from 30% to 40% for the samples prepared at 135°C. Among the samples with different percentages of RAP, those with 50% RAP showed the highest difference in blending efficiency with the change in mixing temperature. A previous study reported that the highest RAP mobilisation rates and subsequent blending efficiencies were obtained at lower RAP content as opposed to higher content [39]. In this study, however, the blending efficiency was seen to be in a similar range for all RAP mixtures and mainly dependant on the temperature of mixing. This could be mainly attributed to the level of ageing and chemical nature of the RAP material. However, the exact influence of these factors is still unknown and is assessed in the next chapters.

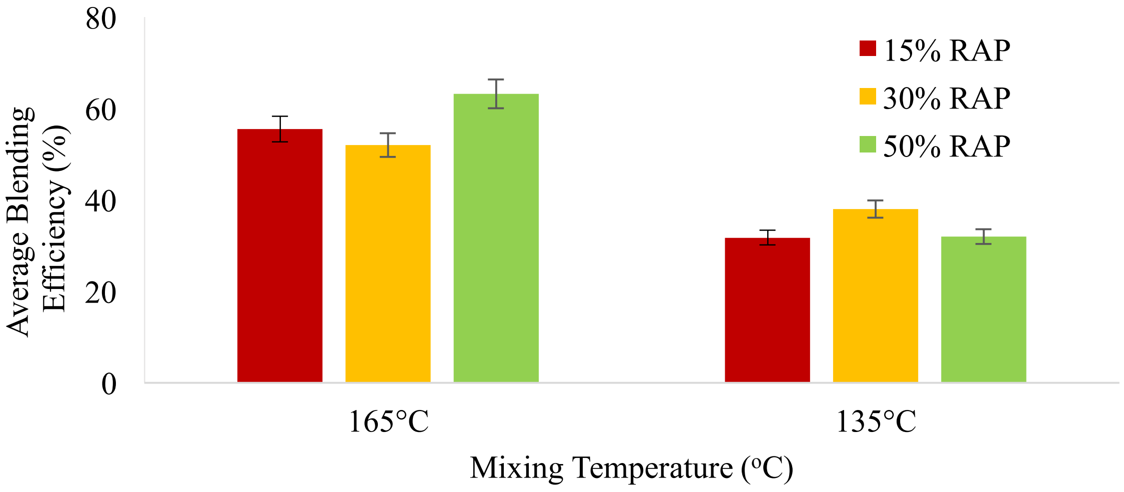


Figure 3.10 Blending efficiency of the control samples

3.6 Validation of the Proposed Parameters

To validate the results attained from the proposed ATR-FTIR method, the rheological and chemical properties of the recovered binders were tested. Frequency sweep tests were firstly conducted to evaluate the rheological properties of the binders using DSR. The rationale for using such tests is that if the higher temperature can mobilise more RAP binder, then the resultant extracted mixture of RAP and virgin binder should be considerably harder and exhibit higher complex modulus |G*| especially at lower frequency ranges [97]. Figure 3.11 shows the G* values exhibited by the RAP binder in comparison to the virgin binder and the artificially blended binders at 15%, 30% and 50% RAP binder contents. It was observed that even 15% RAP binder could have one log increment for the value of G*. When the amount of RAP binder was increased to 30% and 50%, their G* values did not change to a comparable extent. It is worth noticing that this result was acquired from the artificially blended binders. Hence, when considering the reduced blending efficiencies of asphalt mixtures with RAP, the expected differences in G* between the extracted binders are less. Figures 3.12, 3.13 and 3.14 show the frequency sweep tests of the various binder samples prepared at different temperatures and in comparison, to the artificially blended binder of the equivalent RAP proportion. It was observed that for all tests, the samples prepared at higher mixing temperature indubitably showed higher G* values which indicate that those respective binders contain significantly more RAP binder as compared to the samples prepared at a lower temperature. However, the artificially blended binders showed even higher G* values which demonstrate that a normal mixing process cannot obtain the same level of RAP binder mobilisation as artificial mixing. Although these tests cannot quantitatively confirm the results of the FTIR tests, they verified that the approach using the proposed method is representative of the actual mixing that occurs.

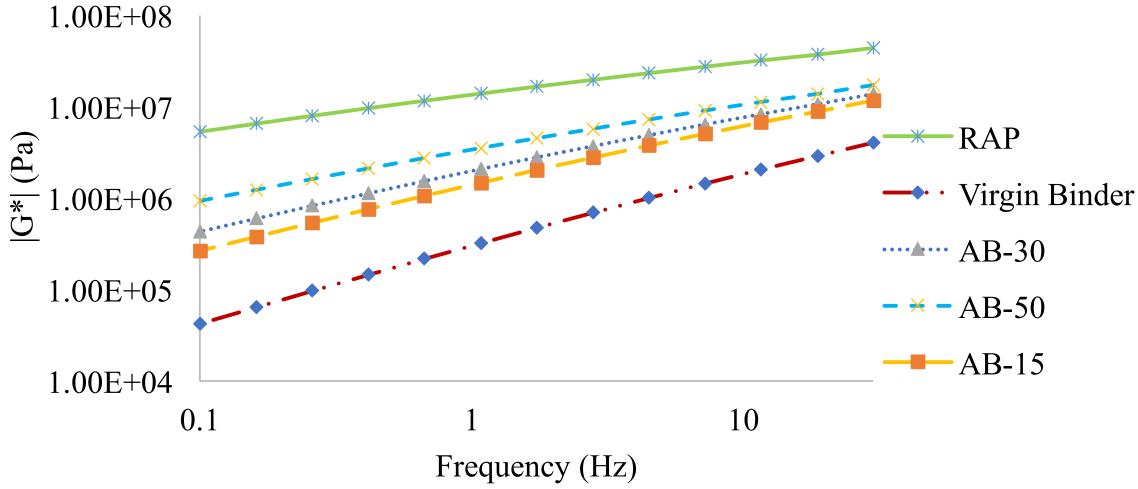


Figure 3.11 Frequency sweep test at 30°C

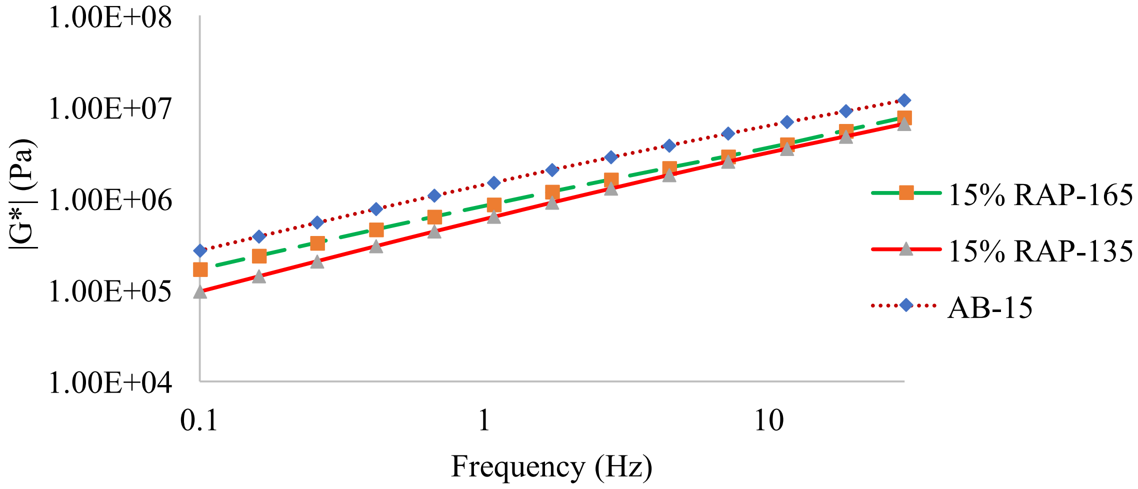


Figure 3.12 Frequency sweep test at 30°C at 15% RAP content

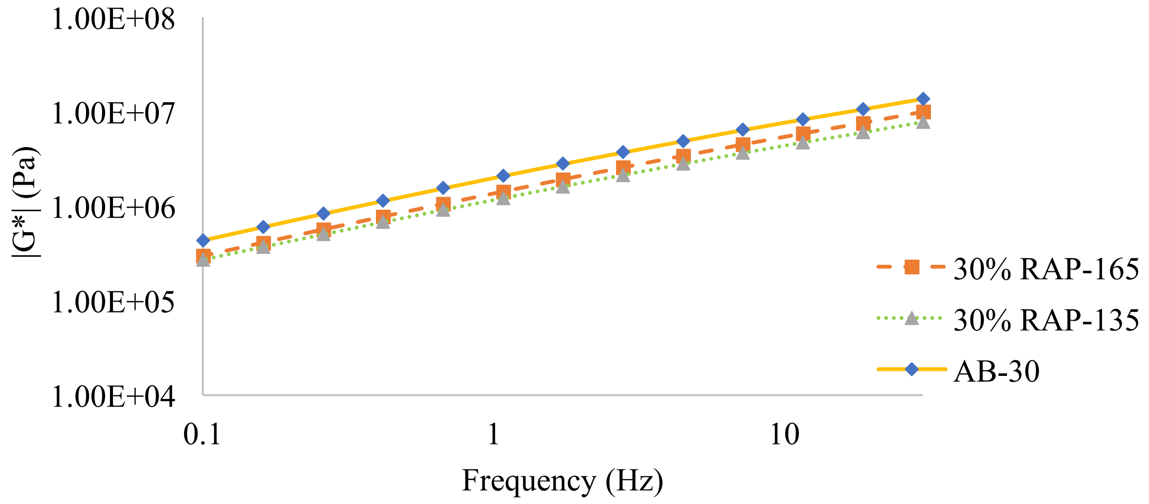


Figure 3.13 Frequency sweep test at 30°C at 30% RAP content

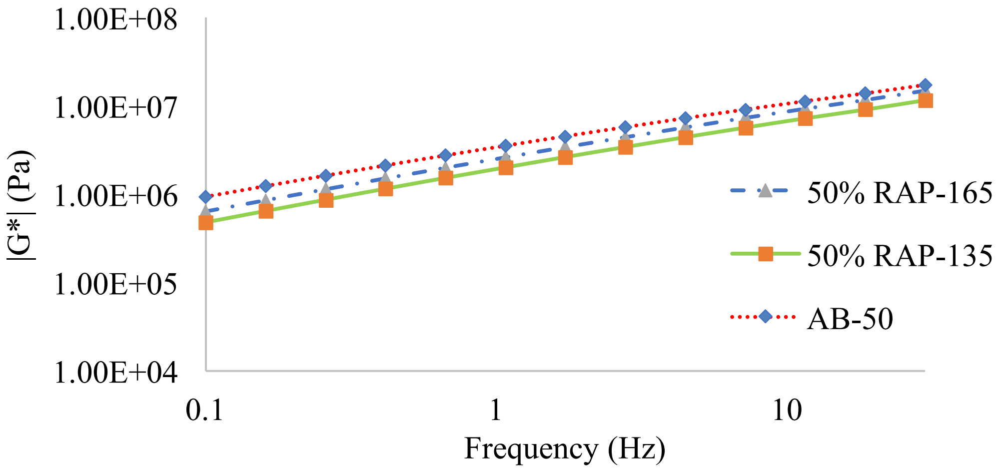


Figure 3.14 Frequency sweep test at 30°C at 50% RAP content

GPC analysis has been extensively utilised in asphalt research in the past and found to be suitable to correlate ageing behaviour of binders. The LMS percentages obtained from the tests have also been successfully correlated with the extent of oxidation and ageing by various studies in the past [97,98]. The chromatogram of the virgin binder and RAP binder is presented in Figure 3.15 and the results obtained using Eq (3.4) for the LMS percentages of the various binders are presented in Figure 3.16. The LMS percentage attained from the RAP binder was 12.5%, which is significantly higher than the value of 5.9% for the virgin binder. For the artificially blended binder with 50% RAP binder, the LMS percentage was 10.9% which is higher than the LMS percentage of 50% RAP-165 sample (10.4%), while the LMS percentage of 50% RAP-135 sample was only 9.8%. The same tendency was found in the LMS percentages of the binders with RAP contents of 15% and 30%. The samples prepared at a higher temperature of 165°C, in general, showed a higher percentage of LMS, which indicates that more RAP binder has been mobilised in those mixtures as compared to the samples prepared at 135°C. But even those samples do not reach the LMS percentage exhibited by the artificially blended samples which suggests that the mixtures prepared cannot reach full efficiency.

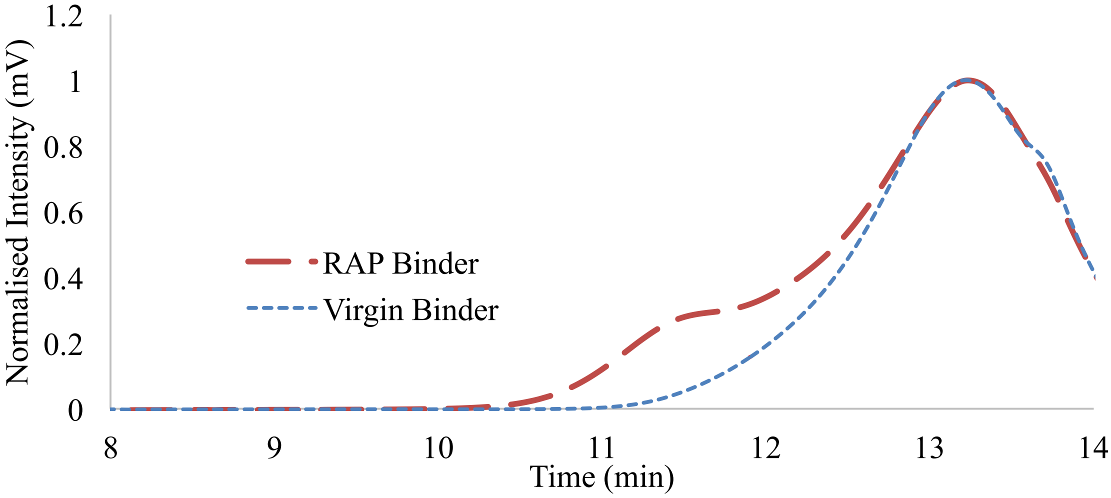


Figure 3.15 Illustrative chromatogram of the RAP binder and virgin binder

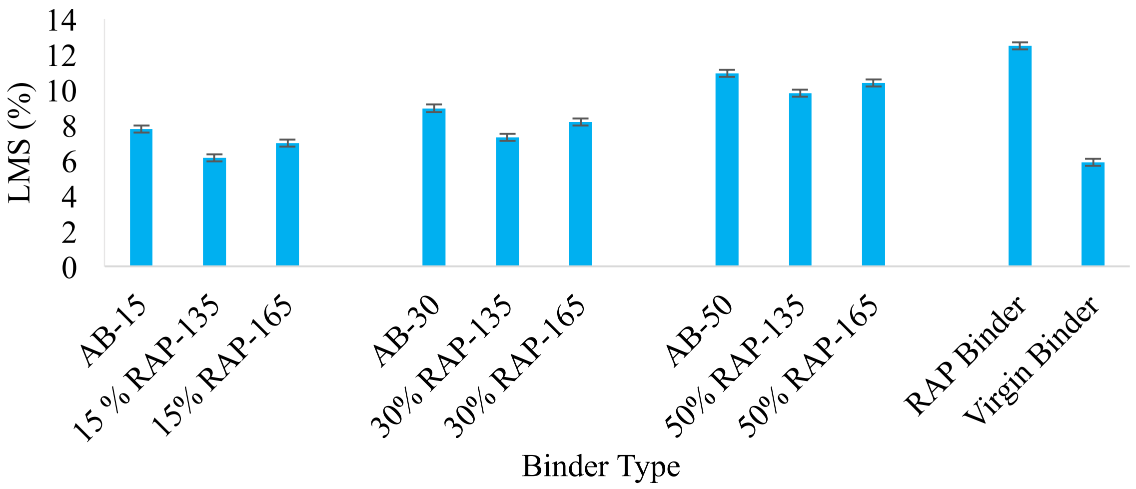


Figure 3.16 LMS (%) obtained from GPC testing

3.7 Conclusions

In this chapter, a novel method is employed to quantify the degree of RAP binder mobilisation and subsequent blending efficiency of RAP mixtures. The following points summarise the chapter:

- Indexes were developed using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy which indicated the degree of mobilisation of RAP binders and subsequent blending efficiency.
- Glass beads of various sizes were used as tracers in mixtures to separate some virgin aggregates from prepared mixtures.
- Mixtures were prepared using the Marshall mix design method using 15%, 30% and 50% RAP content, at two different temperatures.
- Binders were recovered from these mixtures and evaluated using the developed indexes. It was seen that the RAP mobilisation is highly dependent on temperature, the mixtures prepared at 165°C showed on average close to 30% higher RAP mobilisation than mixtures prepared at 135°C.

- These results were validated through the means of dynamic shear rheometer (DSR) and gel permeation chromatography (GPC) tests. Parameters such as complex modulus of binders and large molecular size percentage (LMS %) were used to evaluate the validity of the FTIR indexes.

It is worth noting, though, that the glass beads used in this study do not exactly represent the identical nature and texture of the real aggregates used in bituminous mixtures. Additionally, the blending efficiency parameter assumes full blending to create the efficiency baseline. Although it is useful for practical purposes as per the current understanding of the materials, it may not capture the complete nature of the blending process. Hence this parameter is not considered in the subsequent chapters of this dissertation.

CHAPTER 4

EFFECT OF MIXING VARIABLES ON RAP BINDER MOBILISATION

This chapter is divided into 2 parts. In the first part, the effect of different warm mix additives (WMA) on RAP binder mobilisation was assessed. Following this, the variability of this mobilisation subject to the use of different RAP materials used is evaluated. Analyses were performed on the RAP binders through chemical composition analysis using saturates, aromatics, resins, and asphaltene (SARA) fractionation and microstructural characterisation using optical microscopy to identify the probable mechanism dictating the mobilisation phenomena. Lastly, the implications of these results in terms of the mixing process are discussed.

Portions of the results and discussion presented in this chapter have been previously published in "Evaluation of RAP binder mobilisation and blending efficiency in bituminous mixtures: An approach using ATR-FTIR and artificial aggregate, Construction and Building Materials 179 (2018), 245-253"; "Variability of RAP binder mobilisation in hot mix asphalt mixtures, Construction and Building Materials 201 (2019), 502-509"

4.1 PART A. Effect of Warm Mix Asphalt (WMA) Additives

4.1.1 Background and Types of WMA

One of the issues with using high proportions of RAP in new pavement mixtures is related to the increased stiffness and workability issues. Practitioners have recently started to address this with the utilization of WMA additives, which allows for the construction of pavement at lesser temperatures than traditional HMA by increasing the workability of mixtures. The use of WMA also brings considerable environmental and economic benefits. There are more than 30 different types of WMA products available in the market these days, and can be broadly divided into 3 categories-

- Foaming additive (mechanical foaming and foaming additives)
- Organic additives
- Chemical additives

4.1.1.1 Foaming Additives

The process of foaming requires small amounts of water which is achieved by directly injecting into hot binder or into the mixing chamber. When the water at lower temperatures interacts with the hot binder, it evaporates quickly, and the steam is entrapped. A considerable volume of foam is generated by this effect which results in the rise in the volume of the binder, leading to the reduction of its viscosity. There are mainly two methods used to inject water namely the water-based method (direct method) or water containing method (indirect method) [100]. The former injects the water directly during the blending process of asphalt and aggregate. However, this requires specific equipment to achieve the foaming process. The later on the other hand uses synthetic zeolite-based additives to produce the foaming effect. These are hydrothermally crystallised and contain around 20% of water which can be released as the temperature rises. Commercial products based on this technology mainly include Advera (PQ Corporation) and AsphaMin (Eurovia and MHI).

4.1.1.2 Organic Additives

Organic additives are mainly composed of wax [101]. It is believed that when the mixing temperature rises above the melting point of the additive, there is a decrease in binder viscosity. As the mixture cools, the additives solidify into equally dispersed particles which heightens the binder’s stiffness. However, it has been reported that the addition of such organic additives compromises the low-temperature performance of mixtures as a result of the increased brittleness of the binders. Some of the most commonly used organic additives include sasobit and asphaltan.

4.1.1.3 Chemical Additives

Most of the chemical additives are made from proprietary materials and its constitution varies significantly. It is believed that these additives use chemical energy to replace part of heat energy to improve the workability of mixtures. These additives are known to contain a combination of emulsifying agents, surfactants and polymers which are then added to binders at different dosages dependent on the product used. Some of the reported temperature reductions that can be achieved using such chemical additives range from 15-75^{o}C [101]. Some of the most commonly used chemical additives include Evotherm DAT, Evotherm 3G, and Rediset.

4.1.2 Experimental Mix Design and Materials

The same mix design procedure as the one applied in Chapter 3 was used in this study. The specific gradation of the mixture is presented in Table 4.1 (same RAP source as the one used in Chapter 3). Four different types of commercially available WMA additives were chosen in this study including wax-based, foaming and chemical additives. The details of the additives used are presented in Table 4.2 and Figure 4.1 respectively. As per the same process described previously, glass beads of different sizes that represented a 2% fraction of the mixture were used.

Table 4.1 Gradation of Mixture for WMA Mixtures

	Mixture Gradation	RAP gradation
Sieve Size (mm)	Pass ratio (%)	
14	100	100
10	85.0	94.1
5	58.0	87.8
2.36	38.0	70.0
1.18	26.0	50.2
0.6	17.9	32.7
0.3	11.0	19.2
0.15	3.4	9.7
0.075	3.0	3.4

Table 4.2 Warm Mix Additives Used

Additive Type	Name	Dosage	Legend
Wax Based	Sasobit	1.5% by weight of binder	Saso
Foaming	Asphamin	0.3% by mixture weight	Aspha
Chemical	Evotherm DAT	5% by weight of Binder	DAT
	Evotherm 3G	0.5% by weight of Binder	3G

a) Saso b) Aspha c) DAT d) 3G

Figure 4.1 Pictures of the warm mix additives

4.1.3 Experimental Procedure and Methods

4.1.3.1 Preparation of Samples and Mixing Process

Control mixtures with 15%, 30%, and 50% RAP percentages were prepared at the temperatures of 135°C and 165°C as illustrated in chapter 3. Additionally, mixtures with the same proportion of RAP were also prepared using the warm mix additives at the temperature of 135°C. The WMA was first added to the virgin binder before subsequent mixing with aggregates [102]. After mixing, the glass beads were collected, and the binder was recovered using Trichloroethylene (TCE) solvent. In addition, binders were also prepared by mixing the virgin binder with the recommended dosage of WMA using a high shear mixer for viscosity tests.

4.1.3.2 Viscosity Tests

To measure the viscosities of various warm binders, Brookfield viscosity tests were conducted in accordance with ASTM D4402 using a DV-II Brookfield rotational viscometer. The samples were conditioned in the thermo-container for about 30 min at the chosen test temperature before testing.

4.1.3.3 Method for Evaluating RAP Binder Mobilisation

The RAP Binder mobilisation was estimated based on the method described in the previous chapter using the ATR-FTIR spectra of each binder samples. The integrated areas (IA) under the carbonyl group of each spectrum was used to determine the extent of RAP binder mobilisation. This parameter is used to represent the RAP mobilisation and can be described as follows:

$$\text{Percentage of RAP Binder Recovered (\%)} = \frac{IA_{BS}-IA_{VB}}{IA_{RAP}-IA_{VB}}*100 \quad (4.1)$$

where,

IA_{BS} is the IA of the recovered binder from the respective sample;

IA_{VB} is the IA of the virgin binder;

IA_{RAP} is the IA of the RAP binder.

The binders were examined using a Bruker Vertex 70 Hyperion 1000 spectrometer mounted with a diamond ATR module to obtain this parameter. The spectra of each binder were measured in reflective mode from 4000 to 4 cm^{-1} with a resolution of 4 cm^{-1}.

4.1.4 Results

4.1.4.1 Viscosity

Warm mix additives are generally expected to reduce the viscosity and improve the flow characteristics of the asphalt binders at lower temperatures. Most early WMA literature revolved around this idea and the subsequently reduced production temperature as a result [103]. Before testing for the mobilisation parameter, the viscosities of various binders were measured at the warm mixing temperature of 135^{o}C and at a higher temperature of 165^{o}C as presented in Figure 4.2. It was observed that at 135^{o}C, the warm binders have considerably lower viscosities than the virgin binder. But at 165^{o}C, this difference is less significant. Therefore, the warm binders offer better workability at lower temperatures but as the mixing temperature increases, this effect is less obvious specifically with regard to the virgin binder used in this study. The foaming additive Asphamin was not used in the viscosity study, because its working nature makes it unsuitable for this test.

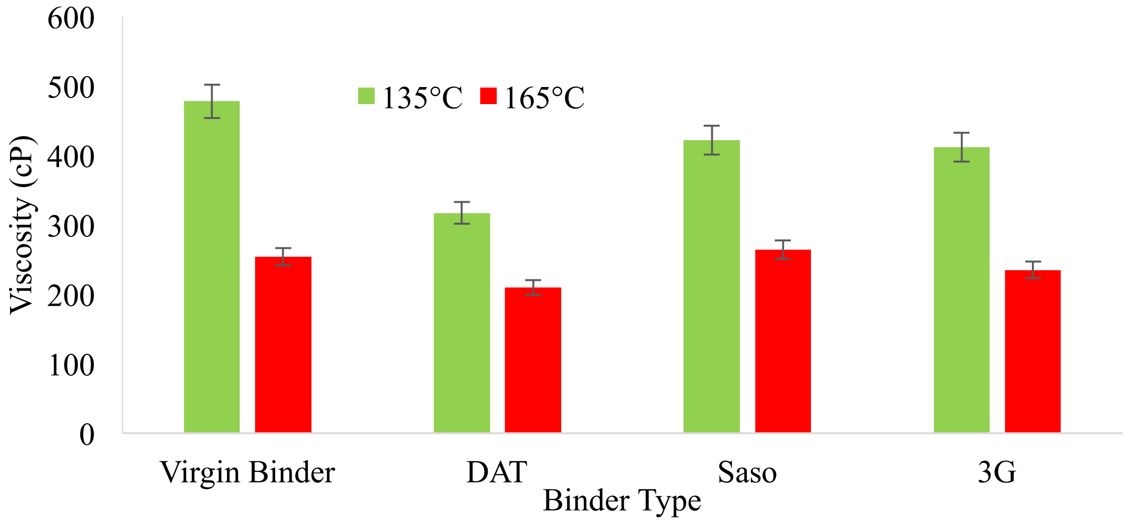


Figure 4.2 Viscosities of the warm binders

4.1.4.2 Effect of WMA on RAP Binder Mobilisation

The recovered binders were tested according to the mobilisation parameter to assess the percentage of RAP binder recovered. As illustrated in Figure 4.3, all recovered warm binders exhibited a higher percentage of RAP binder than the control sample prepared at 135°C. Among different warm mix additives, the chemical additive DAT showed the highest capability to mobilise RAP binder. At 30% RAP content, Asphamin additive also showed higher mobilisation capability than the control sample prepared at 165°C. Asphamin is a synthetic zeolite-based foaming additive which temporarily causes the binder to be smoother and more workable [104]. This effect during mixing could have instigated the increased mobilisation of the RAP binder. Prior studies have also reported similar effects of foaming-based additives on RAP binder mobilisation and blending [95]. When considering the addition of an additive like Evotherm DAT, the increase in RAP binder mobilisation can be expected. Such additives contain a larger number of "surface-active agents" or surfactants that have both polar and non-polar properties. During the mixing process, these surfactants tend to gather at the interface of asphalt and aggregates. The polar parts are attracted by the aggregates and the non-polar part attracts the binder. The surfactant thus acts as a lubricant and allows the binders to easily cover the surface of the aggregate. This will naturally increase the interaction between the RAP aggregates and binder which may induce more RAP binder mobilisation. However, the mechanism of mobilisation is still theoretical at this stage and possibly unique to each additive chemistry. Additionally, as the warm mix additives were seen to have lower viscosities at the mixing temperature, the influence of the overall workability of the mixture on binder mobilisation is also likely. These could have practical implications and are discussed in the next part of this chapter.

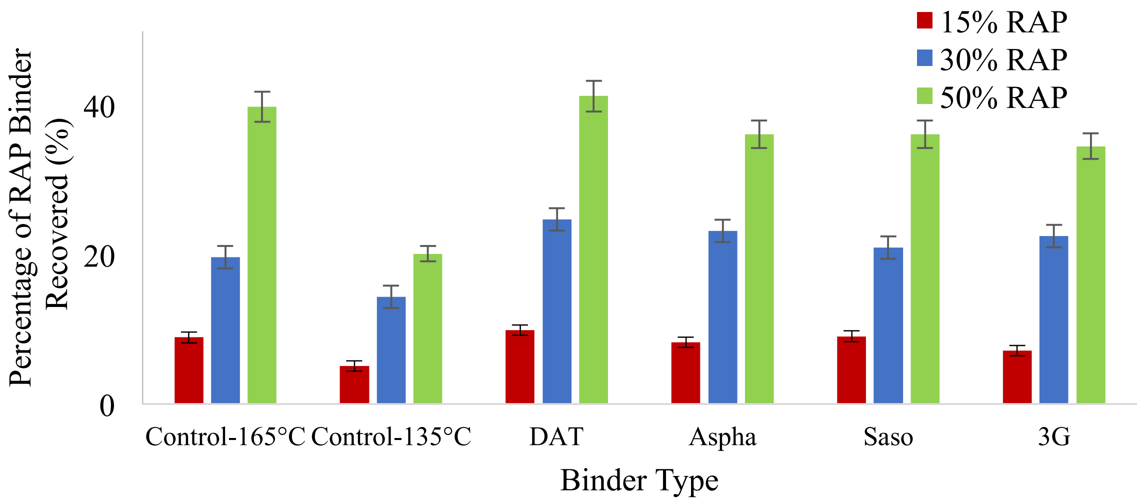


Figure 4.3 Percentage of RAP binder recovered for warm mix samples

4.2 PART B. Effect of RAP Type

4.2.1 Background

When considering the mobilisation and blending of RAP binders, there is significant variability of results available in literature as pointed out in Chapter 2. This indicates that seemingly looking for universally applicable quantitative answers may not be the correct approach as there is considerable inconsistency in materials used when contemplating a highly inconsistent material such as RAP. Nearly all studies conducted so far have characterised the level of blending and mobilisation with the respective materials of the study, while none have analysed their materials characteristics in-depth, which in turn could have prompted the observed results. This is a significant drawback as one of the main material characteristics of importance in a RAP mixture is the specific RAP material used. It is likely that the binders in different types of RAP will be mobilised and blended differently with virgin binders, depending on their specific rheology and chemical properties. This, in turn, will have a considerable effect on the final performance of mixtures. Hence, it is important to comprehend the variability in this mobilisation, and the physical and chemical properties of RAP that may influence it.

4.2.2 Experimental Mix Design and Materials

A similar design method was employed as Chapter 3 but with different RAP materials. The three different sources of RAP were obtained locally from wearing course milling and named RAP-1, RAP-2, and RAP-3, respectively. The specific gradations of the three RAP mixtures are presented in Table 4.3. However, only RAP above 0.6mm was used in this study to prevent excessive clustering of RAP fines. The binders from each RAP were extracted according to the procedure specified in AASHTO T164 and the conventional properties of the extracted binders and the virgin binder are presented in Table 4.4. The mixtures in this study were prepared with consideration of the whole contribution of the recycled binder. AASHTO T308 standard was followed to determine the binder contents of the RAP, which were found to be 5.4%, 5.7 %, and 5% for RAP-1, RAP-2 and RAP-3, respectively. For all the mixtures with 15%, 30% and 50% RAP materials, a total binder content based on the binder content of the respective RAP was chosen. A mechanical mixer was used to mix all the samples for a period of 2 min to reduce variability between samples with regards to preparation. Lastly, as per the same process described previously, glass beads of different sizes that represented a 2% fraction of the mixture were used.

Table 4.3 Gradation of the Various Mixtures

	Mixture Gradation	RAP Gradation (%)		
Sieve Size (mm)	Passing ratio (%)	RAP-1	RAP-2	RAP-3
14.00	100.00	100.00	100.00	100.00
10.00	85.00	90.70	95.60	94.23
5.00	58.00	68.15	73.46	58.87
2.36	38.00	49.02	50.22	35.46
1.18	26.00	33.81	32.73	25.54
0.60	17.90	23.31	21.80	19.32
0.30	11.00	14.84	16.13	14.60
0.15	3.40	8.31	11.96	9.85
0.08	3.00	4.27	6.92	5.42

Table 4.4 Conventional Rheological Properties

	RAP-1	RAP-2	RAP-3	Virgin Binder
Penetration (0.1 mm, 25°C)	34.0	39.0	46.0	69.0
Softening Point (°C)	61.5	57.5	53.5	48.0

4.2.3 Experimental Procedure and Methods

4.2.3.1 Preparation of Samples and Mixing Process

Mixtures with 15%, 30%, and 50% RAP were prepared using each type of RAP and virgin materials. All samples were prepared at the standard hot mixing temperature of 165°C. After mixing with the virgin binder, all the glass beads were collected from the loose mixtures. The binders were removed from the glass beads of each respective mixture as a single entity using trichloroethylene (TCE) solvent for further analysis.

4.2.3.2 Method for Evaluating RAP Binder Mobilisation

The RAP binder mobilisation was evaluated using Eq (4.2) as per the method using the ATR-FTIR described in section 4.1.1 and is not discussed here again.

4.2.3.3 Viscosity

To measure the viscosities of various RAP binders, Brookfield viscosity tests were conducted in accordance with ASTM D4402 using a DV-II Brookfield rotational viscometer. The samples were conditioned in the thermo-container for about 30 min at the chosen test temperature before testing.

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

The SARA fractionation into saturates, aromatics, resins, and asphaltene components was conducted as per ASTM D2007 to determine the chemical compositions of the different binders. In this test, the asphaltenes and maltenes were firstly separated using isooctane. The separation of the maltenes fraction into saturates, aromatics and resins were conducted using a glass liquid chromatography column with chromatographic grade activated alumina. The three fractions were subsequently eluted using different solvents, such as n-heptane, methanol, toluene and trichloroethylene.

4.2.3.5 Optical Microscopy

To study the microstructures of the various binders, a customised optical microscope from Leitz Ergolux equipped with a 100X objective was used, following the procedure described in a previous study [105]. An unmodified version of this microscope is shown in Figure 4.4. The samples were illuminated using a 20W halogen lamp emitting a spectrum peaked at 630 nm. To prepare the testing samples, a tiny amount of binder was placed onto a microscopic slide and then heated to around 140^{o}C using a heater. The heating was stopped once the bitumen melted and flowed. The samples were then left to cool to room temperatures before testing. The detailed setup of the microscope is further discussed in the appendices, section A.3.

Figure 4.4 Optical Microscope

4.2.4 Results

4.2.4.1 RAP Binder Mobilisation

The binders recovered from the prepared mixtures were evaluated using Eq (4.2) and the results are presented in Figure 4.5. It can be seen that RAP-1 and RAP-2 showed similar mobilisation trends, whereas, in comparison, RAP-3 showed higher mobilisation tendencies. In general, the results suggest that the mobilisation of the RAP binder is lesser when the RAP content in the mixture is higher. At 50% RAP content, mixtures prepared with RAP-1 and RAP-2, showed around 20% and 22% of RAP character in the recovered binders, whereas the mixtures prepared with RAP-3 showed a higher percentage of 28%. At all percentages of RAP, the binder in RAP-3 was able to be mobilised at a higher rate as compared with RAP-1 and RAP-2. RAP-3 showed on average around 35% -50% higher mobilisation rate than RAP-1 whereas the difference between RAP-1 and RAP-2 was only around 10%. However, from these results, it can be inferred that a sizeable percentage of RAP binder seems to be unavailable to be mixed with the virgin binder under these mixing conditions. Thus, there is a high possibility of producing under-asphalted mixtures at high RAP contents if full blending is assumed, which may lead to several pavement distresses [106].

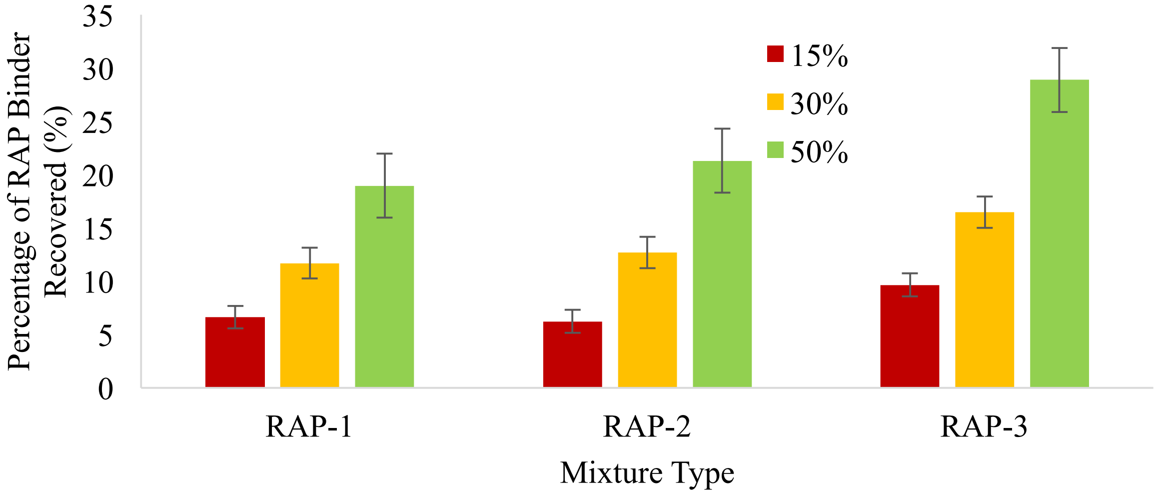


Figure 4.5 Percentage of RAP binder recovered from binder samples

4.2.4.2 Viscosity

It is important to understand the various influences that govern the RAP binder activation process so that specific considerations can be considered to design mixes. One of the most apparent factors that could be involved in the mobilisation process is the workability of the RAP binder. If the RAP binder is unworkable and highly viscous at the mixing temperature, it is unlikely that it would contribute much in a mixing process, especially in order to create a homogenous film around virgin aggregates. Viscosity tests were conducted to evaluate if an obvious relationship existed between binder workability and mobilisation capability, and the results are presented in Figure 4.6. RAP-1 was the stiffest binder exhibiting the highest viscosities at all testing temperatures, followed by RAP-2 and RAP-3. At the mixing temperature of 165^{o}C, RAP-1 had a viscosity of around 540 cP, RAP-2 had a viscosity of 470 cP and RAP-3 had the lowest viscosity of 210 cP. As expected, the RAP binders that are more workable may be more susceptible to be mobilised during a mixing process with virgin binder and aggregate. The viscosity results obtained may also explain the effect observed by other researchers wherein the mobilisation capability increased with temperature, which in essence is a reduction in viscosity and increase in workability of RAP binders [36,38].

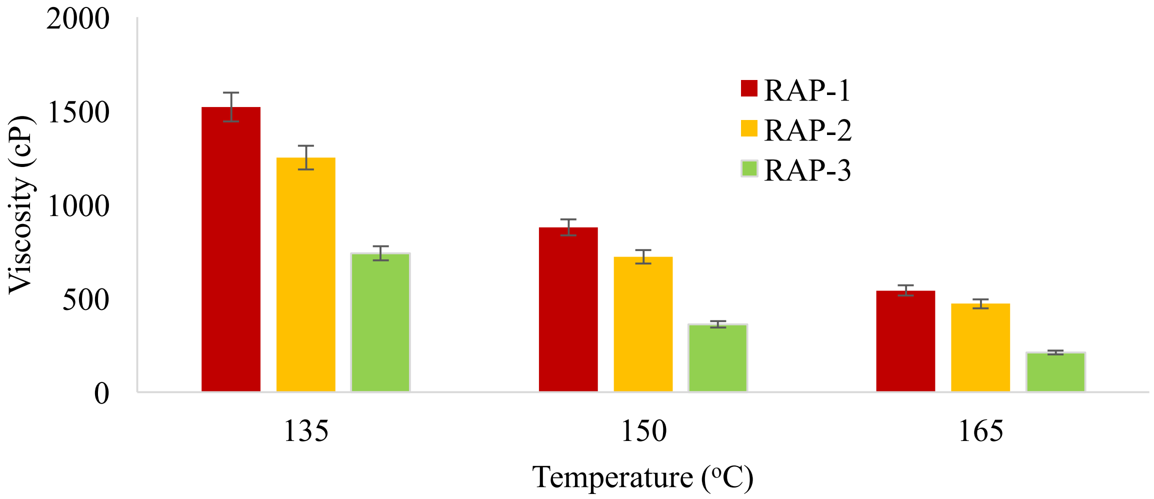


Figure 4.6 Viscosities of RAP binders

4.2.4.3 SARA Fractionation

Although viscosity may be a good indicator of RAP binder mobilisation capability, it can only explain the mobilisation phenomenon partially. In order to fully comprehend the mechanism involved, it is necessary to analyse the materials from microscopic and chemical perspectives. Ultimately, the chemical compositions of binders dictate their field performance when used in an asphalt mixture. The precise chemical composition of bitumen is complicated and impractical to interpret experimentally. As mentioned in the literature review, it is common to separate bitumen into its polar fractions i.e., saturates, aromatics, resins, and asphaltenes, which have shown to have a convincing relationship with rheological properties [107,108]. These chemical fractions represent a continuous spectrum of polar molecules and are not isolated units in the bitumen matrix. Although the original sources of bitumen are different in the case of the RAP binders, the SARA fractions can still give some useful information regarding its chemical nature and polarity-based mobility tendencies. The SARA fractionation for the various binders was conducted as per the method described in section 4.2.3.4 and the results are presented in Figure 4.7.

The ageing of binders generally first leads to a decline in aromatic content and the subsequent increase in resin and asphaltene content. It is hypothesised that the aromatics generate resins which are then converted into asphaltenes [54]. When comparing the different binders, one obvious difference is the asphaltene content. The asphaltene contents of RAP-1, RAP-2, and RAP-3, were 15.89%, 13.24%, and 12.5%, respectively. But as the original fractions of the binders are unknown, it is difficult to suggest any additional correlation other than this deviation, which is known to influence binder stiffness. Moreover, the asphaltenes produced during ageing can differ from those present initially as reported by some studies [82]. The micelles of asphaltene are understood to dispersed in an oily medium of maltenes, i.e., saturates, resin and aromatics. These micelles are thought to be asphaltenes along with a stabilizing layer of aromatic resins of high molecular weight. The viscosities of the maltene components are dependent on the molecular weight distribution. This viscosity accords a fundamental viscosity to bitumen which is then increased by the asphaltene components.

It is interesting to note that the saturate content in RAP-3 was around 24%, which is considerably higher than the other RAP binders. Higher fractions of saturates have been known to soften bitumen as it can increase the inherent mobility of the chemical fractions [54]. Looking factually at the SARA fractions of the different RAP binders, it is reasonable to conclude that RAP-3 will have higher mobile tendencies than the other RAP binders studied here, and this phenomenon would be accentuated with the increase in temperature and mixing time. Although the SARA compositions and viscosity tests can shed some light on the RAP binder activation phenomenon, it cannot however fully explain the specific interaction of the RAP binder with the virgin binder during mixing. This is discussed further in the subsequent part of this chapter.

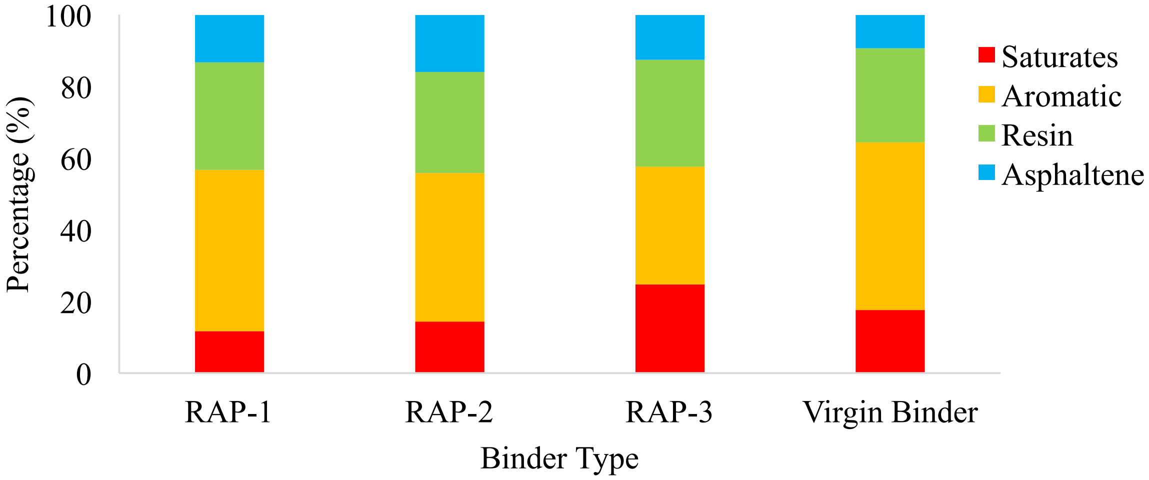
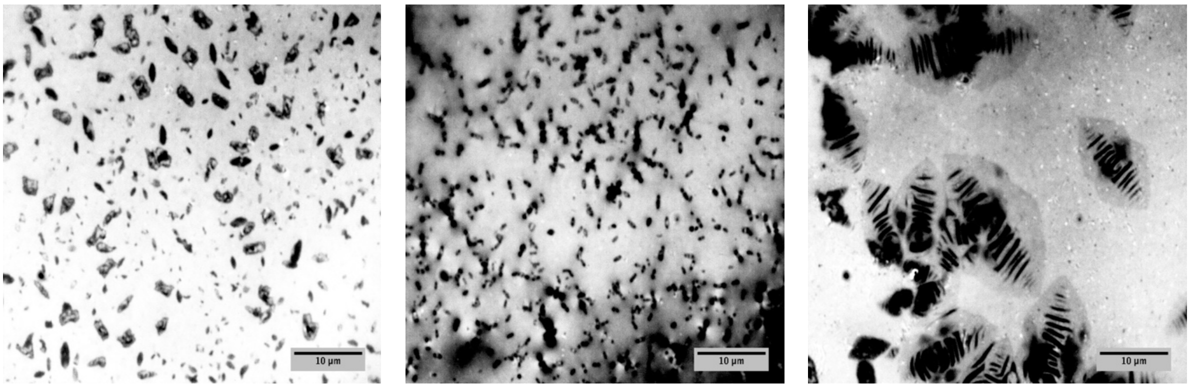


Figure 4.7 SARA fraction of binders.

4.2.4.4 Optical Microscopy

Microscopic studies were conducted using an optical microscope to study the various microstructural features of the RAP binders as illustrated in Figure 4.8. The characteristic distinct domains or “bee” structures were observed in all 3 binders. However, their size, appearance, and dimensions differed significantly. Smaller and less defined bee structures were observed on the surface of RAP-1 and RAP-2, whereas RAP-3 showed more distinct and sharper structures. The bee structures are commonly attributed to the “catana” phase which is known to be surrounded by the dispersed “peri” phase, both phases representing apparent interfacial differences in the bitumen matrix [109]. The exact chemistry and rheology of the phases are still being debated as mentioned in Section 2.7. However, it is believed that the properties of the microstructures influence the bulk properties of the binder, such as stiffness, and viscoelasticity. Long-term ageing has been known to significantly affect the microstructural features of asphalt binders, and the smaller bee structures observed here at 100X magnification are characteristic of aged binders reported in the literature [110]. The appearances of these structures and their differences most certainly depend on different properties of the binder, such as composition and intermolecular mobility. The saturate content of binders has been reported to be a dominant factor causing the appearance of such bee structures as a result of the ratios of the various chemical components in the binders and its effect on the overall polarity at the surface [111]. For RAP-3, the formation of relatively larger structural entities suggests that the mobility of its molecules is relatively higher. Conversely, for the stiffer binders, such as RAP-2 and RAP-1, the structure formation is much smaller and more dispersed. This suggests that either the composition of these binders is not amenable to form structures or the intermolecular mobility is low or both, but their mobility is lower, and they cannot reach their low-energy position, creating indented and detached borders, and hence more domain structures [112]. Examining these differences in light of other information such as the differences in viscosity and relative SARA fractions suggests that RAP-3 has higher molecular mobility compared to the other two RAP binders. It is also important to note that although these structural features are primarily surface entities, it is the macroscopic properties of the bulk that induces these attributes.

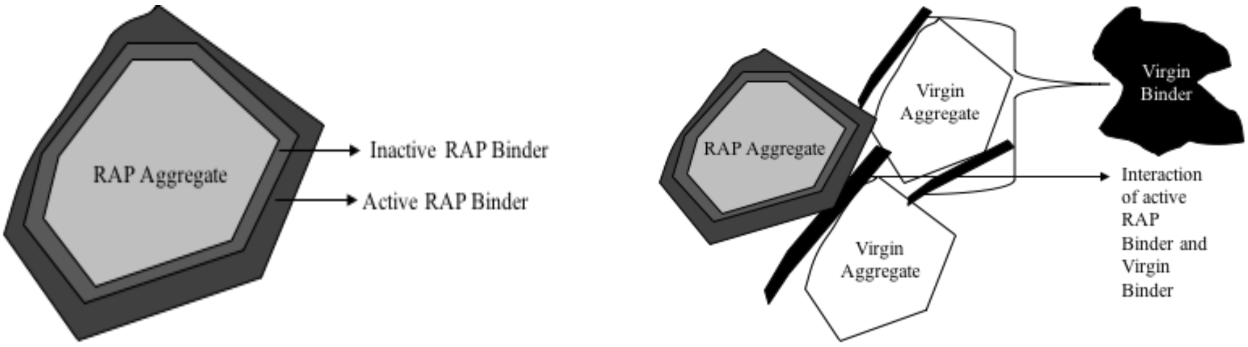


a) RAP-1 b) RAP- 2 c) RAP-3

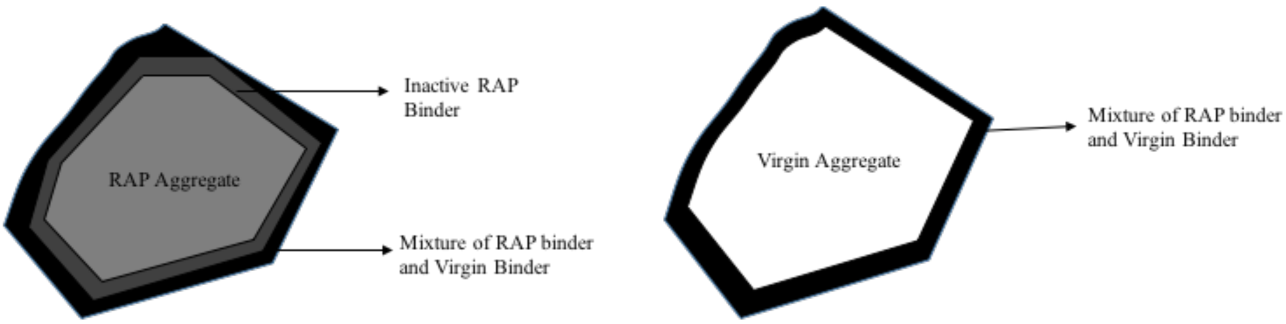
Figure 4.8 Microstructure images of RAP binders

4.3 Mechanism of Mobilisation

From the tests conducted in this chapter, it can be ascertained that in a conventional hot mixing process, the rate of mobilisation of RAP binder is subject to the specific mixing conditions, and also the chemical and rheological properties of the RAP used. Using this understanding, it is possible to predict the mechanism of RAP binder mobilisation in a mixture. As reported by many other researchers, there is likely a layer of active binder that exists around RAP binder which can be mobilised during the mixing process with the virgin binder, as shown in Figure 4.9 [113]. During the mixing process, the mobilised RAP binder interacts with the virgin binder and virgin aggregates to form a binder blend that will subsequently coat all aggregates in the mixture. However, the amount of mobilised RAP binder will differ, contingent on the type of RAP used and other conditional variables, such as temperature, mixing time and overall workability of mixtures, which in principle can also alter RAP properties to induce mobilisation [6, 36].



a) RAP aggregate b) Mixing Process



c) After Mixing

Figure 4.9 Mixing process of RAP with virgin binder and aggregate

Although viscosity may be a good practical indicator at this stage to ascertain the ability of RAP binder to mobilise, it can only partially explain the complete RAP mobilisation and blending phenomenon. It is important to also comprehend the effect of the virgin binder on RAP. In a mixing process, the virgin binder acts as a solvent of sorts and “rejuvenates” the RAP binder. Depending on this interaction or compatibility between the binders, some RAP binder can also be activated in this manner. Further, compatibility between two binders can be defined in terms of solubility. If a virgin binder is completely or partially soluble in RAP binder or vice versa, it is rational to conclude that some RAP binder is mobilised and blended in this process. The solubility parameters for bitumen have been previously described for representing the solubility of solvents in bitumen. However, it can also be applied to appreciate the solubility of various bitumen fractions with each other, which is essentially what occurs during a mixing process [64]. The basis of solubility parameters has been explained in Chapter 2 and can be traced back to the single parameter solubility factor (δ_T), which is based on liquid cohesion energy and molar volume [60]. Single parameter solubility factors can be further divided into Hansen solubility parameters (HSP): dispersion interaction (δ_D $MPa^{1/2}$), dipole interaction (δ_P $MPa^{1/2}$) and hydrogen-bonding interaction (δ_H $MPa^{1/2}$). Using this, the relative solubility between two substances can be estimated using the ‘distance’ between corresponding HSPs in three-dimensional space and referred to as Hansen space [114]. This idea further explored in this the next chapters of this study, including its effect on mobilisation and chemistry of combined blends.

4.4 Findings and Conclusions

In this chapter, the effect of WMA and different RAP materials on RAP binder mobilisation was evaluated using the ATR-FTIR method developed in Chapter 3. Further physical, chemical, and optical analyses were conducted on the RAP binders to understand the probable mechanism that may dictate its mobilisation. The following conclusions could be drawn after the laboratory tests:

- In general, some WMA additives can help to increase the mobilisation of RAP binder as compared to mixtures prepared without WMA at the same temperature.
- Different WMA additives showed different ability to mobilise RAP binder. The RAP mixtures prepared with the chemical additive Evotherm-DAT and foaming additive Asphamin showed the highest tendencies to mobilise RAP binder.
- RAP binder mobilisation considerably varies, depending on the nature of RAP used in the mix. However, a considerable amount of RAP binder remains immobilised regardless of the RAP source.
- The RAP binders exhibiting a lower viscosity at mixing temperature showed higher tendencies to be mobilised.
- From the SARA fractionation tests, no clear trend with mobilisation could be gathered. However, the chemical composition of a binder can indicate the mobilisation potential of its fractions.
- From the optical microscopical studies, it was seen that the binders exhibiting lower viscosity showed a less degraded surface microstructure and higher molecular mobility.
- To fully comprehend the mechanism of interaction and compatibility between RAP binders and virgin binders, solubility parameters or related properties could be useful.

4.5 Implications for Mixture Design

As the quantity of RAP used in mixtures continues to increase, it is critically important for practitioners to consider the actual amount of active and reusable RAP binder available in these mixtures. As seen from the results obtained in this Chapter, there is significant variability in

RAP binder mobilisation differs significantly between different RAP sources and also with the use of WMA additives. Therefore, a one fits all approach may not be appropriate. At this stage, the best practical option suitable would be to use viscosity as a parameter to assess RAP variability. Binders exhibiting high viscosity may be regarded as incompatible to be used as active binder replacement in RAP mixtures or may require special mixing conditions such as increased mixing time and temperature. In terms of WMA additives use in RAP mixtures, no general conclusion for mixture design can be reached. Overall, there is a need to develop specifications exclusive to RAP wherein the amount of residual binder added could be catered to the detailed rheological properties of the RAP used.

CHAPTER 5

COMPATIBILITY OF MIXING AGED AND UNAGED BINDERS

Asphalt binders in bituminous mixtures with reclaimed asphalt pavement (RAP) comprise fractions of both aged and unaged binders, designed to exist as a single entity. However, their mechanism of interaction and blending is still not well understood. In this chapter, a fundamental measure of compatibility between aged binders and unaged binders was evaluated exercising an extension of the HSP model of solubility. Various binders consisting of an unaged binder, RAP 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. These findings were further corroborated by chemical composition analysis based on SARA fractionation. The implications of these findings on RAP binder mobilisation and binder blending are also discussed.

Portions of the results and discussion presented in this chapter have been previously published in "Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility, Fuel, DOI: 10.1016/j.fuel.2019.05.161"

5.1 Background on Bitumen Compatibility and Solubility

During the mixing process in RAP mixtures, 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 it can be argued 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 [64,115]. 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 [36]. As mentioned in the literature review, approaches such as the bitumen solubility model (BISOM) which is a derivative of the HSP model of solubility may be used to gauge the various solubility related tendencies of different binders and the identify the relative compatibility between them.

5.2. 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 labeled 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.

5.3 Experimental Methods and Procedure

5.3.1 Titration Procedure

The titration procedure followed in the study was based on the principle of turbidimetric titrations [66]. 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:

$$\delta = \frac{(\phi^i \delta^i + \phi^j \delta^j)}{(\phi^i + \phi^j)} \qquad (5.1)$$

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 [64]. As the HSP represents 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. Table 5.1 shows the HSP of the solvent, non-solvents, and bitumen. The HSP of bitumen is based on an average of 15 different binders as reported in the literature [116]. Isooctane, 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 5.1. The HSP sphere details the solubility of bitumen in Hansen space [114] and can be calculated using the following equation:

$$Ra^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \qquad (5.2)$$

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 5.1 HSP of Toluene, Titrants and Bitumen

	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)
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

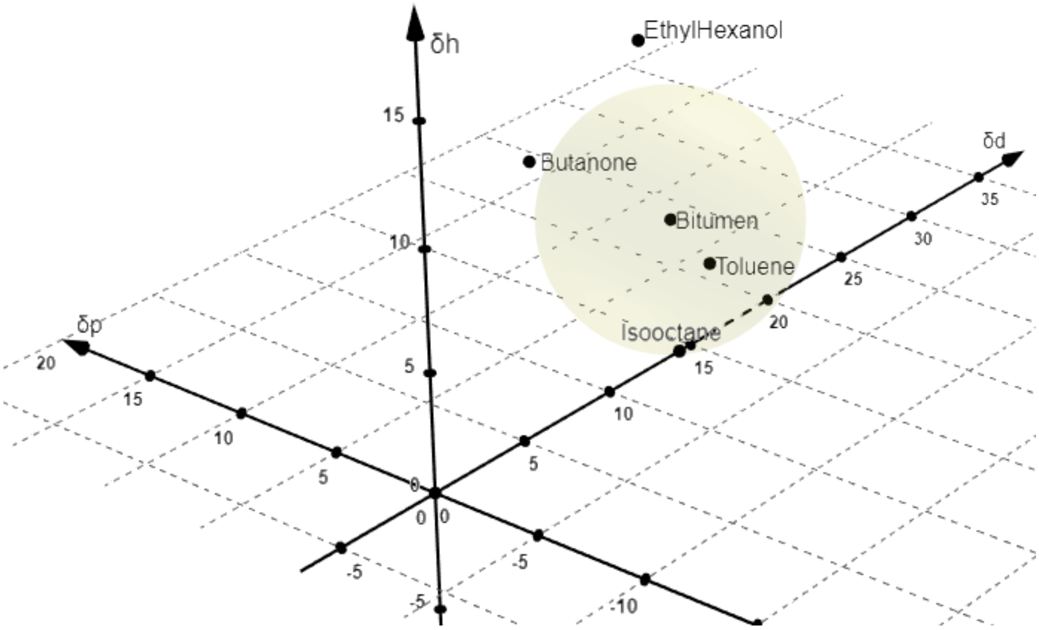


Figure 5.1 HSP of toluene and titrants in the HSP sphere of bitumen

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 [117], 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 work 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 [65]. Figure 5.2 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.

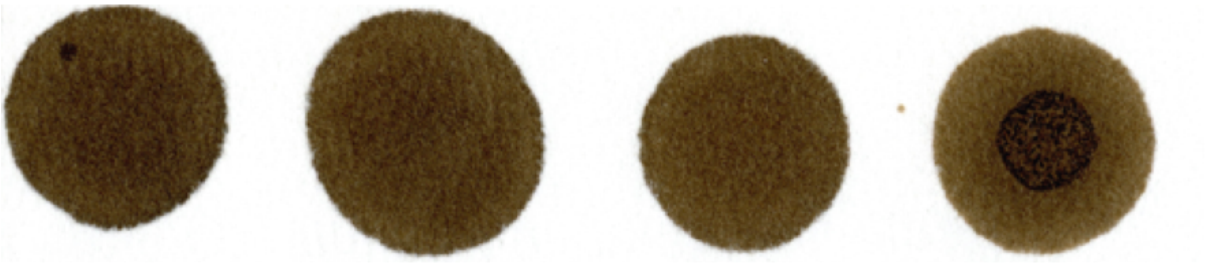


Figure 5.2 Images on filter paper after the addition of each aliquot of titrant (left to right)

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 5.3 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.

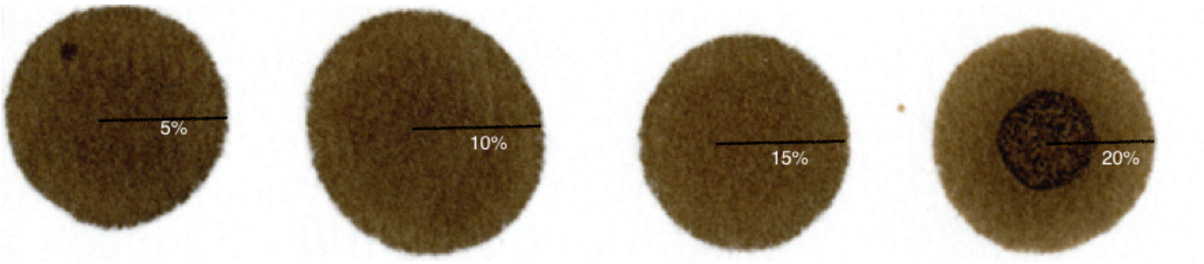


Figure 5.3 Colour intensity analysis of titration results

After determining the flocculation point for each titration, two parameters, namely flocculation ratio (FR) and concentration (C), were calculated using the following equations [117]:

$$FR = \frac{V_S}{V_S + V_T} \qquad (5.3)$$

$$C = \frac{W_A}{V_S + V_T} \qquad (5.4)$$

Where Vs 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. 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 C_{min} is related to the stability of the respective bitumen [118]. Figure 5.4 illustrates the extrapolation technique.

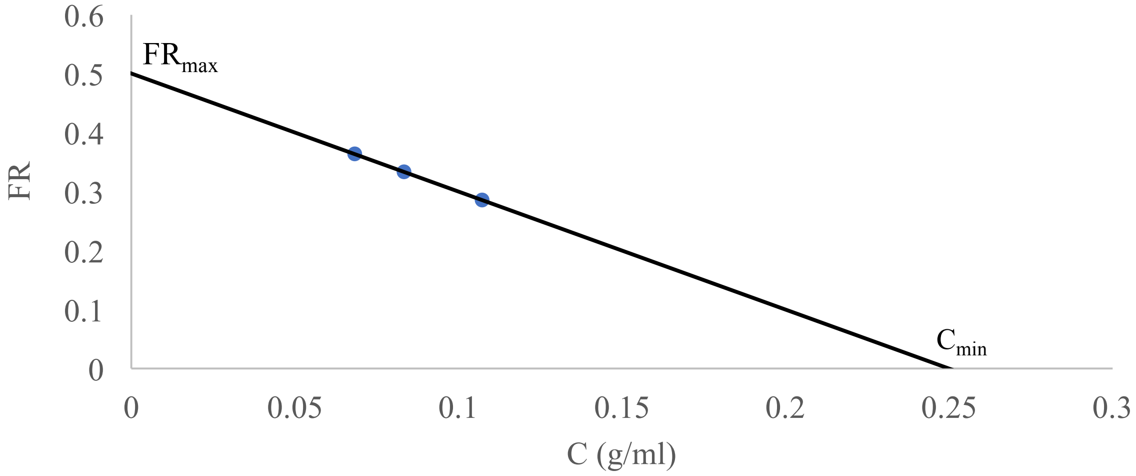


Figure 5.4 Extrapolated graph of FR vs C

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:

$$D_a = 1 - FR_{max} \qquad (5.5)$$

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:

$$D_0 = FR_{max} \left[\left(\frac{1}{C_{min}}\right) + 1\right] \qquad (5.6)$$

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:

$$D = \frac{D_0}{1 - D_a} \qquad (5.7)$$

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.

5.3.2 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, and different from the standard ASTM method presented in Chapter 4 [119]. This method, which is divided into two parts, was developed at the University of Texas at Austin and referred to as "TexSARA". The first part was the solubility-based separation of asphaltenes and the extraction of maltenes. The second part was a 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 polytetrafluoroethylene (PTFE) based syringe filters of pore size of 0.2 μm. This method of asphaltene-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 the action of gravity and vacuum. Figure 5.5 shows a sample elution of the aromatics fraction through SPE cartridges at three different phases. The detailed procedure regarding this method is presented in the appendices, Section A.4.

Figure 5.5 Elution of aromatics through SPE cartridges [119]

5.4. Results and Discussion

5.4.1 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 5.6 (RAP binders and virgin binder) and Figure 5.7 (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 the relative strength of these interactions are represented by the D, H and N parameters shown in the figures.

5.4.1.1 Dispersive Forces

Based on the results presented, one substantial difference between the unaged binder and aged binders is 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 [64]. As mentioned in Chapter 2, the dispersive interactions in bitumen can also be derived mathematically from electronic polarizability and refractivity using the following equation:

$$\alpha = \left(\frac{3}{4\pi N_A}\right)\left(\frac{M}{d}\right)\left(\frac{n^2-1}{n^2+2}\right) \qquad (5.8)$$

Where,

N_A = Avogadro's number,

M = Molecular weight,

d = Density and

n = Refractive Index.

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 [50].

5.4.1.2 Polar and Hydrogen Bonding Interactions

The most notable difference between aged and unaged binders in terms of intermolecular forces is polar interactions, which is expected to 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 the field, especially in terms of UV ageing, which has been shown to appreciably alter the chemistry of binders in terms of polarity [120].

At the molecular level, polarity is the separation of charge within a molecule. All of the naturally occurring heteroatoms, such as nitrogen, sulphur, and oxygen, contribute to bitumen polarity. Upon ageing, the oxidation products formed are polar and further contribute to the overall polarity of the system [57]. 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 5.8 [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 numbers 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 [121]. 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 the blending and stability of the combined binders. This will be discussed in detail in the next sections.

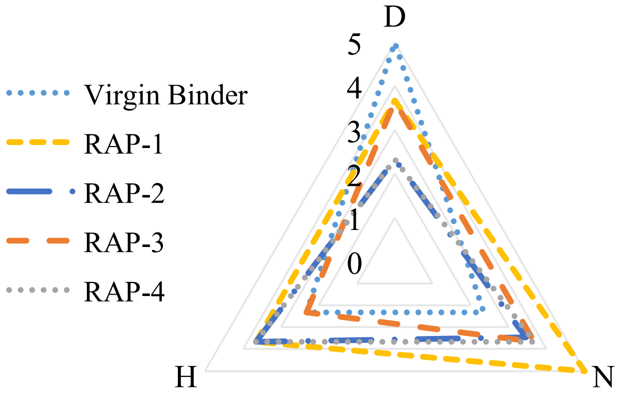


Figure 5.6 Strength of intermolecular interactions in RAP binders and virgin binder

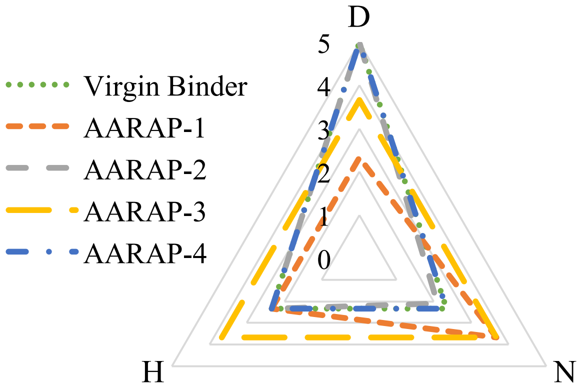


Figure 5.7 Strength of intermolecular interactions in artificially aged binders and virgin binder

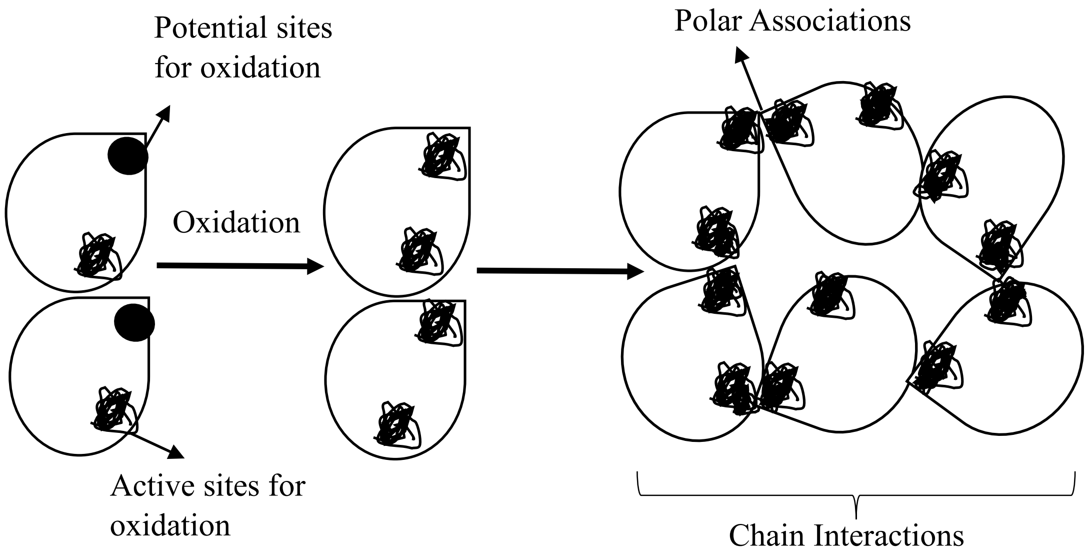


Figure 5.8 Polar associations between molecules

5.4.2 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 [122]. 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 through 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 [37]. Further, the extent of this mobilisation has been shown to be variable, dependent on many 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. 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 dictate the extent to which the aged binder is activated, mobilised and blended with the virgin binder. Furthermore, the 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 [123]. 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 temperatures and mixing time in order to mobilise it and achieve a homogenous blend.

5.4.3 SARA Fractionation

The SARA fractions of the various binders were determined as per the method described and the results are presented in Figure 5.9. 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 the literature [54]. 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 a 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 the blending of different bitumens is established [54].

The ranking of bitumen fractions by the increase in polarity is saturates, aromatics, resins, and asphaltenes. The ageing of bitumen generally first leads to a decline in aromatic content and the 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 [124]. 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 [119]. 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 [125]. Studies on the binder energies for unoxidized and oxidized asphaltene dimers have shown that the total values of intermolecular interactions are stronger for oxidized forms as opposed to unoxidized forms and hence expected to increase agglomerations, leading to the hardening of bitumen [126]. The effect of these increased agglomerations when considering mixing aged binders with unaged binders is a relevant influence that needs to be deliberated.

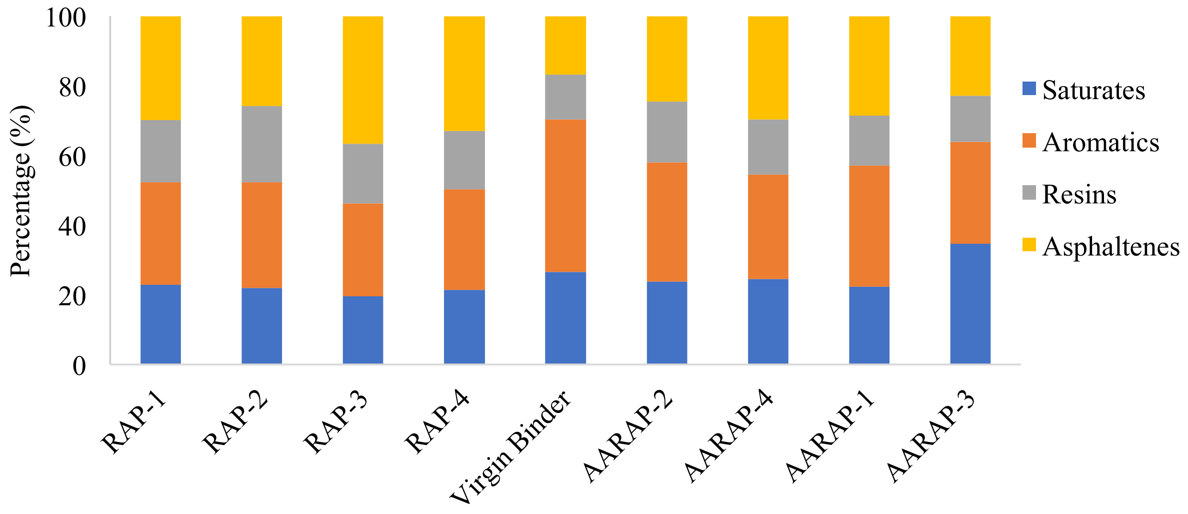


Figure 5.9 SARA fractions of binders

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

From the results obtained from the BISOM parameters and SARA fractionation, aged binders and virgin binders are fundamentally different in terms of chemical composition and intermolecular interactions. These differences are consistent with the broad understanding of the materials established in the 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 [127]. The 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 most well dispersed and stable when all contributing segments have similar solubility parameters. The underlying concept around this being the correlation between cohesive energy density and mutual miscibility [128]. 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 an increase in polarity [128]. 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 the variability 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 [88]. Viscosities of asphalt mixtures of blends have shown irregularities when compared with the viscosities of the original asphalt binders. 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 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 [127]. 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. The next chapter evaluates the detailed chemistry and interaction mechanism between new and aged binders in combined blends of RAP binder and virgin binder.

5.5 Findings and Conclusion

In this chapter, 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 tests:

- The turbidimetric titration method using the selected titrants effectively detected the differences between aged and unaged binders in terms of relative internal stability and intermolecular 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. This is discussed in the next chapter of this dissertation.
- A limitation of this procedure is 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.

CHAPTER 6

CHEMISTRY OF COMBINED BLENDS AND IMPLICATIONS ON BLENDING

In this chapter, an investigation into the interaction mechanism between new and aged binders in binder blends was conducted. Various blends comprising fractions of aged and unaged binders were evaluated using a method of turbidimetric titrations, to identify their internal stability and relative extents of intermolecular interactions in terms of dispersive forces, hydrogen bonding, and polar interactions. Further chemical and rheological tests were conducted using FTIR, GPC, and DSR to evaluate the unique chemistry and rheology of combined blends. Using these results, the possible interaction mechanism between aged and unaged binders and its effect on mixture design are discussed

6.1 Background

One of the most significant limitations that prevent higher use of RAP is the lack of information concerning the variables involved in the blending of aged binder in RAP with the virgin binder during the mixing process. Even though many studies have been conducted regarding these issues, no conclusive and commonly applicable results have been found [37]. 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 blend [37]. The mixing of aged and unaged bitumen is an intricate chemical process and involves the molecular interaction of various bitumens fractions that come together to form new associations. It is also important to bear in mind that aged bitumens are also markedly oxidized 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 [120]. These changes increase the relative extent of polar fractions in these binders leading to the possibility of amplified associations among its molecules [121]. It is reasonable to expect that mixtures of virgin and aged binders may exhibit different extents of intermolecular interactions in comparison to the original sources as a result 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. In fact, such a fundamental understanding is also vital to engineer recycling agents, modifiers and other alternative materials that can be used as a binder extender. As seen in Chapter 6, binders of varying ageing levels when evaluated using a modified BISOM titration method showed that aged binders and virgin binders could differ noticeably in terms of intermolecular interactions [129].

6.2 Materials

Two different 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 virgin binder used was a commonly used local binder of PG high-temperature grade of 64 and low-temperature grade of -12^{o}C. Artificially blended (AB) mixes of the binders were prepared by blending the virgin binder with three different proportions of RAP 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, and the blended binders were labelled as AB-15-1, AB-30-1 and AB-50-1 for the binders prepared using RAP-1 and AB-15-2, AB-30-2 and AB-50-2 for the binders prepared using RAP-2 respectively. All chemicals used in this study were of laboratory grade purchased from Thermo Fisher Scientific. It is well recognized that the complete blending of virgin binder and RAP binder is dependent on temperature, mixing duration, and other factors. However, it is important to note that the goal of this study was not to emulate field blending, rather study the compatibility of blends.

6.3 Experimental Procedure and Methods

6.3.1 BISOM Titration

The titration was conducted as per the method described in section 5.3.1 of Chapter 5 and is not repeated here again. Using this method, parameters D, H and N were obtained which refer to the relative extents of intermolecular interactions in terms of dispersive interactions (D), polar interactions (N) and hydrogen bonding interactions (H).

6.3.2 FTIR Spectroscopy

The FTIR tests were performed on the samples to identify the differences in oxidation exhibited between them. The carbonyl band (C=O) exhibited around 1700 cm^{-1} of an FTIR spectrum was used to quantify the oxidation of different binders [37]. As per the method, as mentioned in Chapter 3, the analysis approach of the various 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:

$$\mathrm{IA}=\int_{w_{l,oa}}^{w_{u,oa}} VA_{norm}(w)\, dw \qquad (6.1)$$

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 defined from the wavelengths of 1666 to 1746 cm^{-1} [94]. The binders were characterized through ATR-FTIR analysis 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

6.3.3 GPC Tests

The GPC tests for the various binders were conducted as per the method described in Chapter 3 to characterise is complete molecular weight distribution. Tetrahydrofuran (THF) was used to dissolve the binders to the required concentration and subsequently filtered through a 0.2 μm filter for testing with a Shimadzu Prominence GPC system using two styragel columns. The large molecular size (LMS) percentages of the samples were calculated from each GPC chromatogram as follows [98]:

$$\text{LMS\%} = \frac{\text{Area of first } \frac{5}{13}\, of\ chromatogram}{\text{Toal Area below the chromatogram}} * 100 \qquad (6.2)$$

6.3.4 Dynamic Shear Rheometer (DSR)

DSR was used to evaluate the rheological behaviour of the various binders. For binders containing recycled materials, the low and intermediate temperature characteristics are of particular concern, as a result of the increased likelihood of cracking in these very stiff materials. The Bending Beam Rheometer (BBR) is most commonly used for low-temperature characterization 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 [130]. 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 [131]. Temperature-frequency sweeps were run at temperatures ranging from -18°C to 40°C and frequencies ranging from 0.1 Hz to 15 Hz. The master curves for each were constructed at a reference temperature of 0°C as per the time-temperature superposition principle. The master curve was created using a sigmoidal function as follows:

$$\log(|G^*|) = \delta + \frac{\alpha}{1+e^{\beta-\gamma\log(t_r)}} \qquad (6.3)$$

where $|G^*|$ = the complex 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. It is indeed 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 shed a better fit in the region of interest.

6.4 Results and Discussion

6.4.1 Solubility based Molecular Interactions

The parameters related to the various molecular interactions in the Hansen model were calculated as per the titration procedure. 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 6.1 and Figure 6.2 respectively. It was seen that both RAP binders displayed noticeably different extent of interactions as compared to the virgin binder. Similar findings were reported in a previous Chapter and ascribed the differences in interactions as a result of the increased molecular associations and agglomeration [57,129]. The increase 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 [129]. As a result, the increased associations among molecules are known to lower its dispersibility thereby 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 fatigue and thermal cracking performance [1,36].

When comparing the artificially blended (AB) binders, the results were varying. In general, the AB binders showed different D, H, N values as compared to the RAP binders and virgin binder. This is expected as AB binders are a combination of its constituents and will naturally have different chemical compositions in comparison. The AB binders are anticipated 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, intermolecular interactions in binders comprise molecular recognition and host-guest interface in 3D porous networks [132]. 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, the binders incorporated with 15% RAP showed results that were similar to the virgin binders. It can be inferred that the inclusion of the aged binder at lower proportions has a limited influence on the internal stability of the virgin binder. In terms of the solubility based 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 displayed lower values for D as compared to the virgin binder which could imply that the stability of those binders are lower than the virgin binder. It must be noted that these changes in internal stability cannot specify that any binder is superior to another but can only indicate a relative difference, which will evidently have chemical and rheological consequences Previous studies have indicated that exhibiting very low values for D, such as the aged binders in this study may exhibit low peptizability and could be thermodynamically unstable [64]. In addition, the binder AB-50-2 also showed an increase in the N parameter as compared to AB-50-1. This can be attributed 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 at small concentrations of RAP, there is not a significant change in the solubility related molecular interactions of the binders. This may have noteworthy implications in terms of practice and are discussed further.

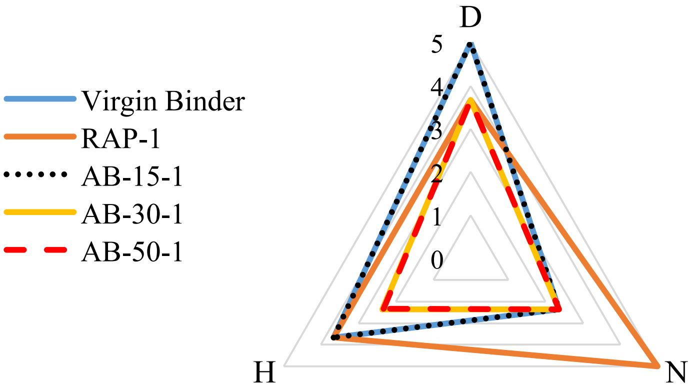


Figure 6.1 Strength of intermolecular interactions in Series 1

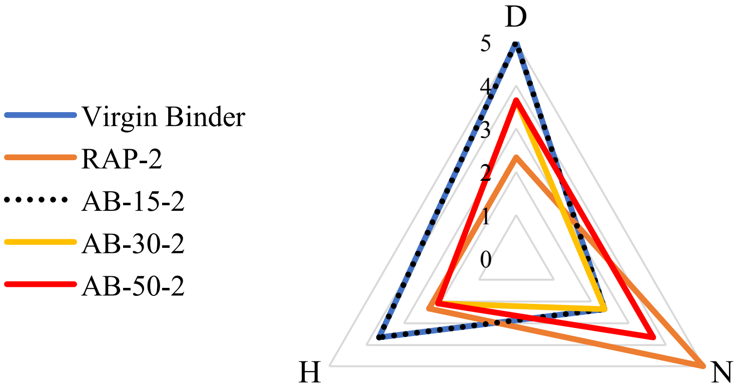


Figure 6.2 Strength of intermolecular interactions in Series 2

6.4.2 Extent of Oxidative Groups

The areas corresponding to the carbonyl bonds were calculated as per the procedure described and the results are shown in Figure 6.3. 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 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 [133]. 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 illustrated in Figure 6.4 [26]. 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 oxidation 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 [133]. More polar, oxygen-containing functionalities are expected to exist in the RAP binders which propagate the agglomeration of certain fractions such as asphaltenes [86,125]. When a small proportion of RAP binder is mixed with the fresh binder, the total oxidative products in the combined binder are slightly increased. However, from the solubility results, it can be seen that the internal stability of the binders stayed relatively similar. Alternatively, at higher concentrations of RAP binder, the internal stability of the combined binder changed 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 associated with 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

[135]. The extent of this interaction will naturally depend on the concentration of the aged fractions in the mixture and will hence vary with concentration.

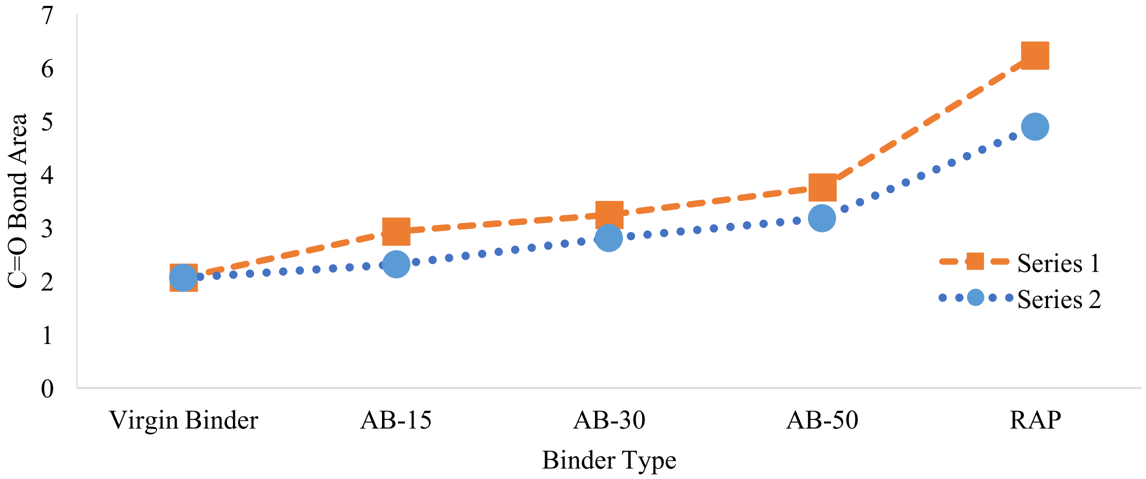


Figure 6.3 Areas corresponding to the Carbonyl Bonds

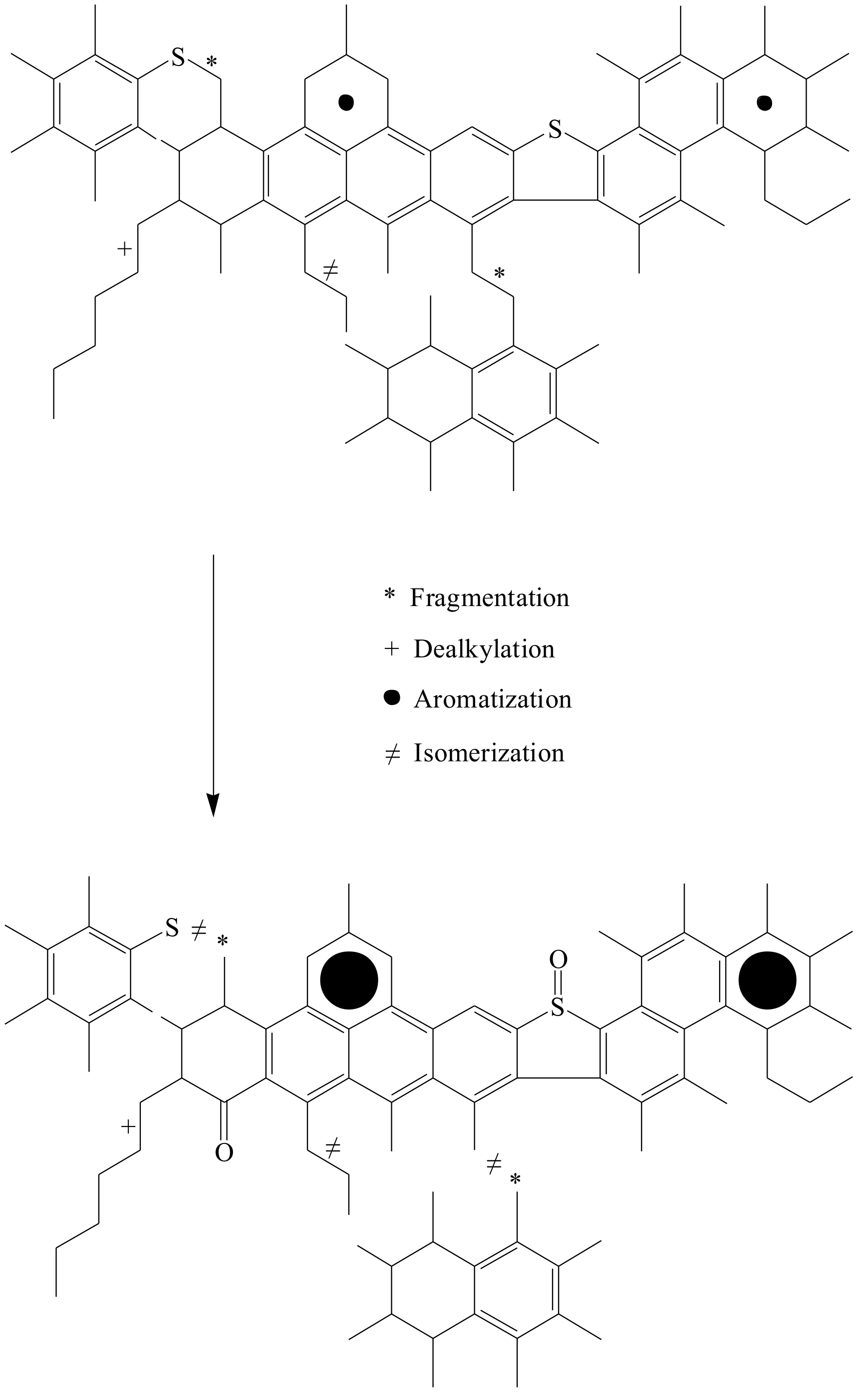


Figure 6.4 Reaction types of bitumen during ageing [134]

6.4.3 GPC Parameters

The LMS fractions of the binders were calculated as per the procedure described in Section 3, with the results represented in Figure 6.5. Prior studies have shown that fractions containing higher extents of the oxidation products are mainly represented in the LMS fraction of the GPC chromatogram [36]. This is mainly attributed to the association of smaller molecules with higher polarities during aging, which then contribute to the LMS fraction [136,137]. It is important to understand the premise of molecular size distribution in bitumen. Bitumen consists of a continuum of fairly large hydrocarbons with different sizes and polarity, with the lowest size of hydrocarbons defined by the respective processing requirements of crude [50]. 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 levels of LMS were seen to increase in the AB binders 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 molecules. 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 represented in Figure 6.6 [138,139]. 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 strong affinity towards non-oxidized asphaltenes via hydrogen bonding, acid-base interactions, and π-π stacking. The addition of such oxidized fractions would facilitate the further agglomeration of molecules, the formation of larger aggregates and reduction of its overall polydispersity [135]. This is shown in the diagram representing the interaction mechanism as shown in Figure 6.7. 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 the 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.

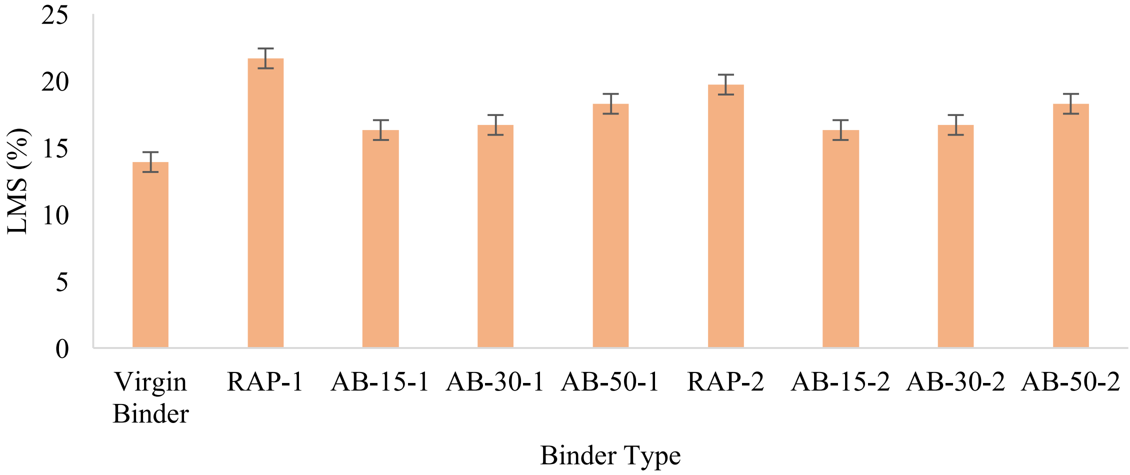


Figure 6.5 LMS (%) obtained from GPC testing

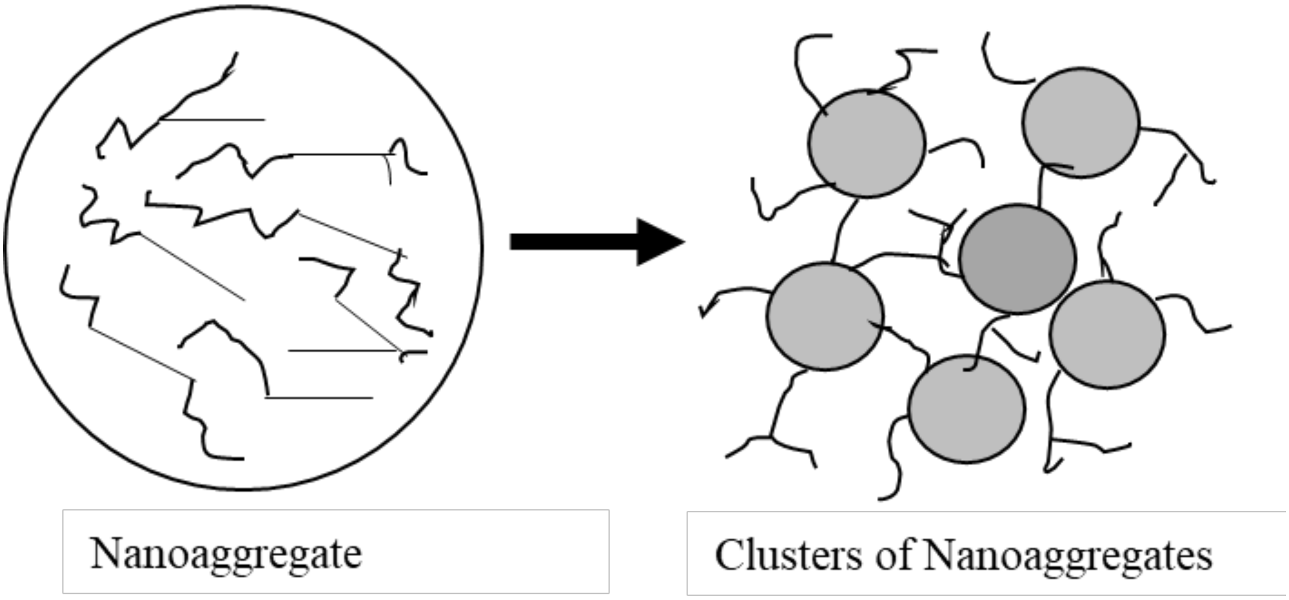


Figure 6.6 Formation of clusters in asphaltene molecules

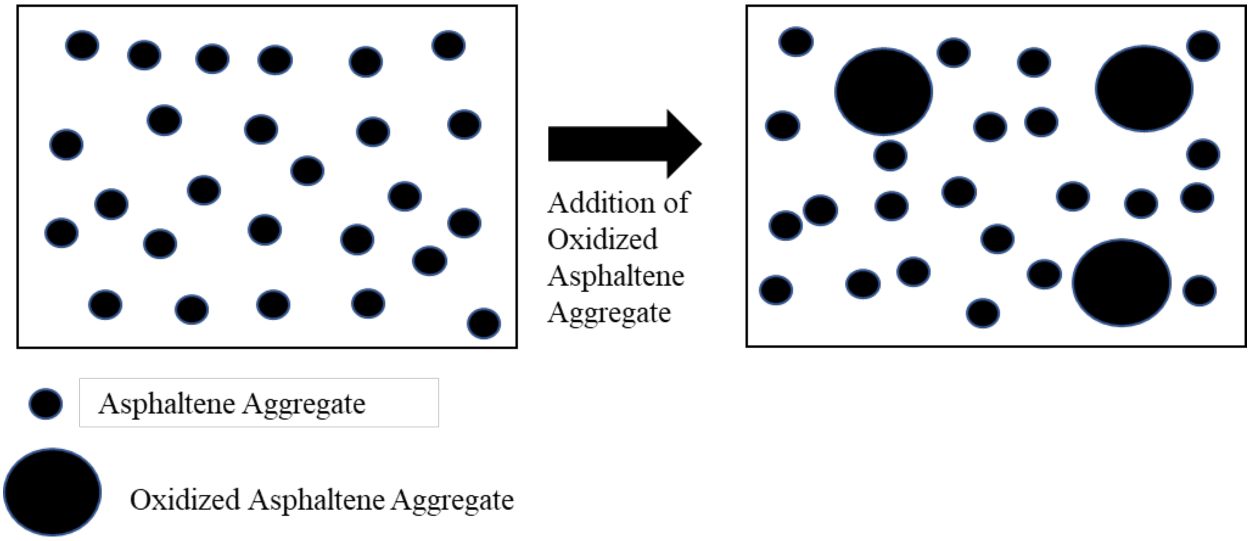


Figure 6.7 Mechanism of change in aggregation during mixing

6.4.4 Rheological Results

The rheological parameters of the two sets of binders were measured as described in section 6.3.4, and the respective master curves are shown in Figure 6.8 and Figure 6.9 respectively. At the 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 high 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 and it increased to approximately 3 for AB-50. In general, the rheological results are consistent with the above parameters in that they exhibit an increase in the bitumen stiffness as higher ratios of RAP binder are used. One possible mechanism for the rise in stiffness is through the increase in particle attraction or π-π interactions [133]. This type of increase in modulus is heightened by the particle sizes and reduced by the dispersing action of the asphaltenes. All molecules are attracted to each other through fundamental forces of attractions and associate with each other. Importantly, 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 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. Such an increase in modulus can be predicted by Einstein's theory of colloids and further modifications based on the Pal-Rhodes model [140,141].

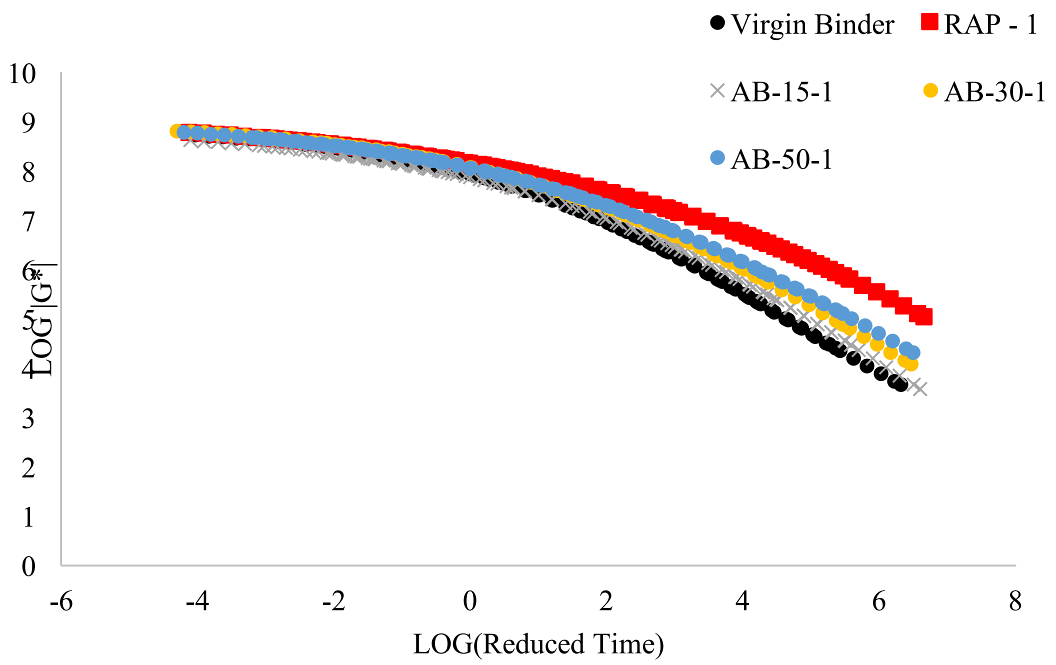


Figure 6.8 Master curve for binders in Series 1

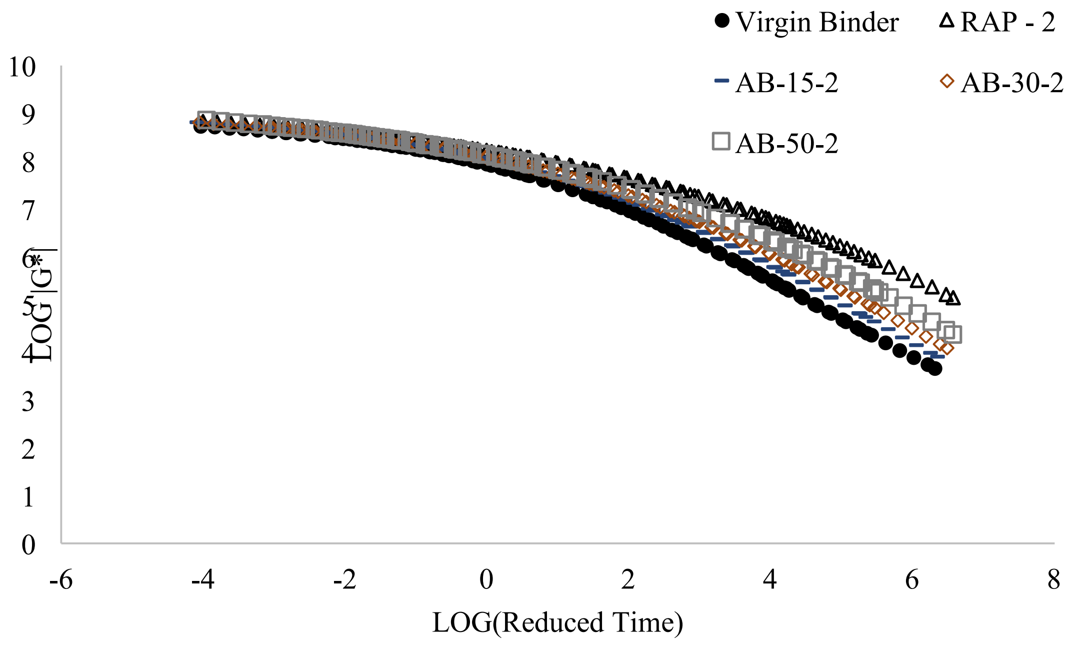


Figure 6.9 Master curve for binders in Series 2

6.5 Findings and Conclusion

In this chapter, the differences in solubility based molecular interactions and internal stabilities were examined for unaged binders modified with different concentrations of RAP binders from two sources, using an extension of the Hansen model of solubility. The following findings were drawn from laboratory tests:

- Binders modified with low percentages of RAP binders showed similar extents of internal stabilities and relative molecular interactions as compared to the unaged binder.
- Increased concentrations of RAP binders altered the extent of relative molecular interactions in the combined blends and are consequently expected to have implications in terms of binder compatibilities and blend homogeneity.
- 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.

- Low contents of RAP may be incorporated into mixtures without any change in mix design. However, using higher RAP content in mixes should ideally involve some consideration of the chemistries of the intermixing binders, in order to design a stable and appropriate blend.

6.6 Implications 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 complicated. 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. 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 [129]. 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 and extent of molecular interactions 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 [127]. These differences could lead to performance issues for the binder that is not accounted for by the rheological parameters. Currently, there are no standards or frameworks for evaluating the compatibility between binders and further research is required in this area.

CHAPTER 7

FINDINGS AND RECOMMENDATIONS

Asphalt binders in bituminous mixtures with RAP comprise fractions of both aged and unaged binders, intended to exist as a single entity. A significant apprehension in the design of such mixtures is the undetermined extent of aged (RAP) binder that is mobilised during mixing, and the ensuing blending of aged and unaged (virgin) binders. The level of this blending is theorized to control the extent of homogeneity of the binder in the mix, and consequently has an important role in the overall mixture performance. This dissertation research aims to systematically investigate and improve the fundamental understanding of the many facets involved in the mobilisation of RAP binder and the subsequent interaction of RAP binders and unaged binders. The first part of the dissertation was focused on developing a new method to evaluate RAP binder mobilisation using ATR-FTIR spectroscopy as a major assessment tool. After this, the effect of important variables in mixture design such as mixing temperature, the addition of WMA additives and RAP type were assessed. Chemical tests such as SARA fractionation and microstructure analysis using optical microscopic techniques were used to concurrently identify the possible mechanisms involved in the process. In the second part, the compatibilities between aged and unaged binders were evaluated using an extended version of the HSP model of solubility which described the variations in intermolecular forces between unaged and aged binders in terms of dispersive interactions, polar interactions, and hydrogen bonding interactions. Lastly, the chemistry of combined blends of aged and unaged binders was studied in terms of internal stability and polydispersity of molecules.

7.1 Findings

Based on the outcomes of the various studies conducted, the following major findings were obtained:

- ATR-FTIR can be used to indicate the extent of mobilisation of RAP binders in bituminous mixtures with RAP.
- RAP binder mobilisation is greatly dependent on temperature. The mixtures prepared at 165°C showed on average close to 30% higher binder mobilisation than mixtures prepared at 135°C.
- In general, WMA additives can increase the mobilisation of RAP binder when compared with mixtures prepared at the same temperature without WMA additives. From the additives tested, specific foaming and chemical additives showed the highest capability to mobilise RAP binder in mixtures, which were comparable to the levels of HMA mixes.
- RAP binder mobilisation considerably varies, depending on the specific RAP used in the mix. However, a considerable amount of RAP binder remains immobilised regardless of the RAP source, under normal mixing conditions.
- The RAP binders exhibiting a lower viscosity at the mixing temperature showed higher tendencies to be mobilised.
- Chemical and microstructural features of a RAP binder can indicate its potential to be mobilised in a mixture.
- Unaged binders and RAP binders may noticeably differ in terms of the extents of relative molecular interactions as per solubility-based parameters. Hence, they are projected to have varying extents of mutual compatibility.
- Special mixing requirements such as increased temperature and mixing conditions could improve the relative compatibility between binders, in relation to RAP binder mobilisation and blending.

- When considering combined blends of RAP binders and unaged binders, binders blended with low percentages (of up to 15%) of RAP binders showed similar extents of internal stabilities and relative molecular interactions as compared to unaged binders.
- Increased concentrations of RAP binders altered the extent of relative molecular interactions in the combined blends, and are subsequently expected to have implications in terms of blend homogeneity.
- 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.

7.2 Conclusions

From the different studies conducted in this dissertation research, the following general conclusions can be drawn:

- There is substantial variability in RAP binder mobilisation as it is affected by various mixing conditions such as temperature, use of WMA additives and use of different RAP materials. The viscosity of RAP binders is expected to be a useful parameter to assess and standardize this variability.
- Through an extension of the HSP model of solubility, the relative molecular interactions of aged and unaged binders in terms of dispersive interactions, hydrogen bonding interactions and polar interactions can be approximated. It was seen that certain unaged binders and RAP binders can vary in terms of the relative extents of molecular interactions. This, in turn, is believed to have implications for the mobilisation of RAP binder, and subsequent blending of RAP binders and unaged binders.
- Low concentrations of RAP binders are anticipated to have a limited effect on the internal stability of combined blends of RAP binder and virgin binder. However, high

concentrations of RAP binders could alter this stability and requires a closer consideration of the intermixing binders.

7.3 Future Work

The phenomenon of RAP binder mobilisation and the subsequent blending of RAP binder and virgin binder in bituminous mixtures is a complex process that involves numerous variables. On the basis of the findings of this dissertation, future study is recommended in the following areas:

- This work only evaluated some important criteria that may affect RAP binder mobilisation and blending. Other parameters such as the effect of aggregate shapes, use of rejuvenators, clustering of RAP fines should be further investigated.
- Specifications could be developed for RAP based on specific rheological parameters such as viscosity. This may help generally improve the blending of binders and improve mixture performance. However, to achieve this, research with a wide database of materials would be required.
- RAP binder mobilisation and blending research are suggested to be applied to the asphalt mastic and fine aggregate matrix (FAM) level, as the interaction the binders could be influenced by the presence of filler.
- Although the solubility-based tools may be useful for research purposes, its practical use may be limited for practitioners and engineers. It is suggested to develop more directly applicable tools to study the molecular interactions and compatibility between a wide array of binders with different compositions. Molecular dynamics (MD) simulation may be useful in that aspect to generate a broad spectrum of data.

LIST OF STANDARDS MENTIONED

AASHTO T164, Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot Mix Asphalt (HMA), American Association of State and Highway Transportation Officials (2014).

AASHTO T308, Standard Method of Test for Determining the Asphalt Binder Content of Hot Mix Asphalt (HMA) by the Ignition Method, American Association of State and Highway Transportation Officials (2018).

AASHTO T240– 09, Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt, American Association of State and Highway Transportation Officials (2017).

ASTM D 6521, Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV), ASTM International, West Conshohocken, PA (2019).

ASTM D2171 Standard Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer, ASTM International, West Conshohocken, PA (2018).

ASTM D2007, Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method, ASTM International, West Conshohocken, PA (2016).

ASTM D5 Standard Test Method for Penetration of Bituminous Materials, ASTM International, West Conshohocken, PA (2019).

ASTM D36 Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus), ASTM International, West Conshohocken, PA (2014).

ASTM D4402 Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer, ASTM International, West Conshohocken, PA (2015).

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APPENDICES

A.1 General Procedure and Notes on the ATR- FTIR Method

A Bruker Vertex 70 Hyperion 1000 spectrometer that holds a diamond ATR module was used to acquire the spectra of the various binder samples. The module was cleaned with trichloroethylene (TCE) solvent and lint-free tissues before and after spectra acquisition. As traces of solvent may be detected by the FTIR, it is important to make sure all solvent has evaporated from the sampling interface. The interface can be further cleaned with acetone after cleaning by TCE. Consequently, the reproducibility of the background spectra can be checked to confirm the identical environment for each test.

In terms of testing, a small amount of binder was taken and placed onto the FTIR optics. To confirm that the test specimen remains in good contact with the optics, a constant pressure may be applied using the ergonomic clamp mechanism of the device. The corresponding spectra of each binder can be then recorded in reflective mode from the wavelength of 4000 to 400 cm^{-1} at a resolution of 4cm^{-1}, using 24 scans for every measurement. Following the tests, the specimen was removed and cleaned as stated above. Generally speaking, careful testing with an experienced operator can produce reproducible spectra that require no baseline correction.

The spectral data were then normalised using the asymmetric stretching vibration of the aliphatic structures exhibited at 2923 cm^{-1}. For normalization, the value of absorbance is set to 1 and the full spectrum is augmented by a ratio factor. The normalisation is based on the following equation.

$$A_{norm}(v) = A(v).\frac{1}{A(2923cm^{-1})}$$

A $_{norm}$(v) is the normalized absorbance spectrum; A (v) is the original absorbance spectrum; A (2923 cm^{-1}) is the original absorbance value at the reference band.

An example of the original spectra and normalised spectra is shown in Figure A1.1.

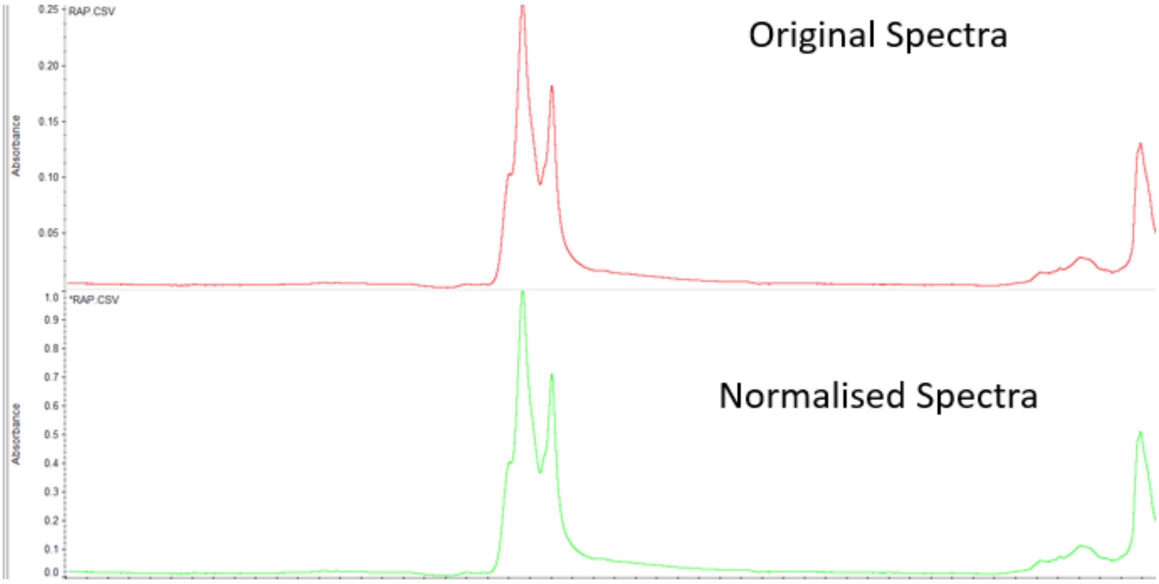


Figure A.1.1 Original spectra and normalised spectra

The analysis approach of the carbonyl band (C=O) exhibited in the various FTIR spectra utilised the integration of areas, normalised spectra (as stated) and an absolute baseline. The evaluation was conducted using OriginPro statistical software. The “integrate” option under the Tools menu was used to calculate the area under the spectra from the wavelength 1666 to

1746 cm^{-1} using an absolute baseline. Figure A1.2 shows an example of the calculated area.

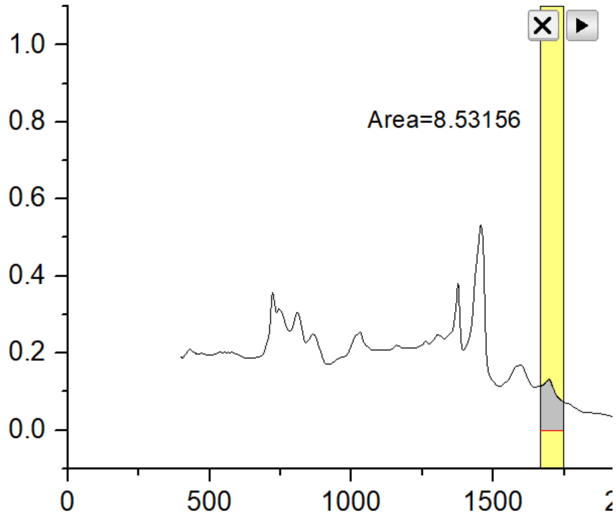


Figure A1.2 Calculation of Carbonyl band area

A.2 General Procedure and Notes on the GPC Procedure

A Shimadzu Prominence GPC system using two styragel columns was used to conduct the GPC studies for the various binders in this study. Laboratory consumables for the GPC tests include-

- Auto sampling vials
- Scintillation vials
- Auto sampling cap crimp
- 0.2 Micron filters
- Syringes
- Tetrahydrofuran (THF) solvent

A concentration of 1mg/ml of binder to the solvent was used to inject the sample solutions into the GPC system. Sample solutions at the desired concentrations were prepared in scintillation vials using a small quantity of binder (10-15mg), and appropriate ml of solvent. The density of THF (0.8892 g/ml) is used to determine the amount of solvent required to prepare the solution of the desired concentration. Following this, approximately 3ml of the solution is transferred into an auto-sampling vial by attaching a 0.2-micron filter to filter the solution through. The samples were then placed into the GPC system and named using the installed software program.

The analysis of the GPC data is relatively simple and can be conducted primarily using MS-excel and OriginPro software. The large molecular size (LMS) percentages were calculated for the binders as follows:

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

However, prior to the calculation of the LMS%, some pre-treatment and normalisation of data are recommended. Correction of datasets can be conducted using the “baseline model” under the peaks and baseline option in the OriginPro analysis toolbar. The dataset is then smoothed using the smoothing option in the analysis toolbar using the “Savitzky-Golay” method. Lastly, the intensity is normalised relative to the highest data value.

A.3 General Procedure and Setup of the Optical Microscope

The optical microscope technique described in this dissertation followed the procedure described in a previous work, developed at the University of Texas at Austin [105]. To study the microstructure of bituminous binders, a customised optical microscope from Leitz Ergolux equipped with a 100X objective was used. The specific set up components of the microscope included:

Heater stage

The heater stage is used to control the temperature of the sample during microstructure imaging. The heater is mounted on translation stages so that it, and the sample, can be moved in the x and y-direction. To get precise temperature control, a thermoelectric heater is connected to an aluminium sample-holder custom-designed for microscope slides. The heater’s temperature range was -10 to 125 °C with 0.1 °C resolution. The heater temperature was monitored and changed with a controller and cooled with continuous water flow, supplied by a 5-gallon reservoir.

Camera

A CMOS camera was used to take images. CMOS is silicon-based, so the light collection range was ~ 300-1000nm. This range worked well for surface and bulk measurements of 500 nm and 850nm respectively. The camera was manually triggered with the included camera software and used an Arduino control board to set up automated triggering.

Objective

A Nikon 40X long working distance objective was attached to the CMOS camera. The long working distance is crucial for the incident beam to be able to reach the sample without being blocked by the objective. Higher or lower magnification lenses could be used, based on the area of the sample under investigation. The scattered light is very weak relative to the incident light (typically ~1x10−8 of incident intensity), so high numerical aperture objectives (typically NA > 0.5) are needed to collect as much scattered light as possible.

Light source

A 250-watt halogen lamp mounted in a custom-built fiber bundle coupler was used as the light source. The halogen lamp was chosen because of its wide spectrum. Intensity at 850nm was much less than at 500nm, however, it proved to be bright enough to observe bulk microstructure scatter. Much higher intensities can be achieved with NIR laser sources, but it was found that interference effects due to scattering of coherent light then complicate interpretation of the images.

Optomechanics

Linear translation stages were used for the sample and objective movements. In order to keep the incident light constant at the objective's object plane, the objective and the focusing lens were fixed in place in the x-y direction. The heater stage was mounted on translation stages in the x-y direction and a z-axis jack. This allowed for a 3-dimensional sample movement. The objective was also mounted on a z-axis translation stage to allow for fine focus control. Figure A3.1 shows the translation stages and setup of the microscope.

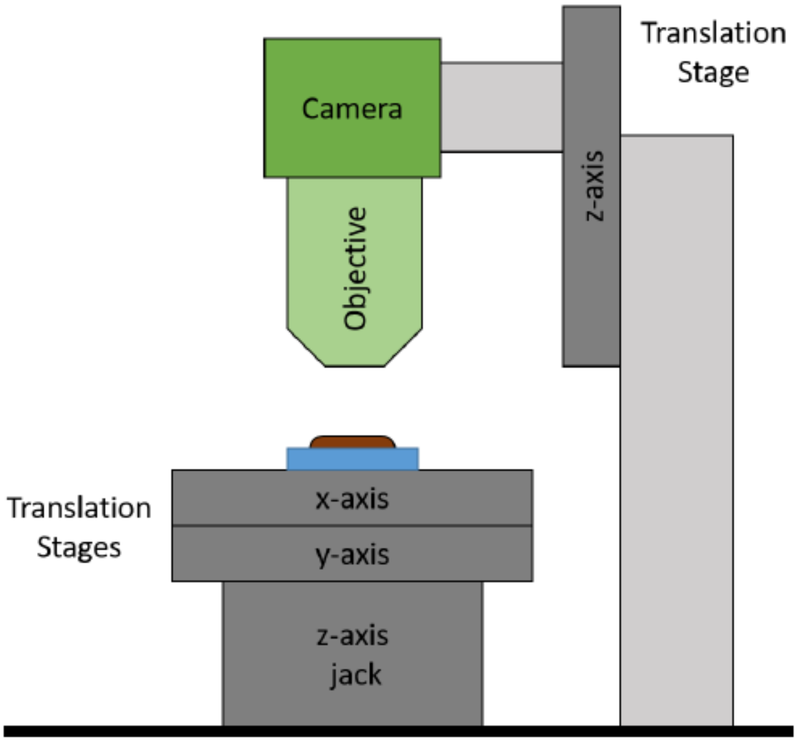


Figure A.3.1 Translation stages for sample and objective movement

A.4 General Procedure and Notes on Tex(as)SARA Procedure

The SARA fractionation method conducted in Chapter 5 of this dissertation was conducted as per the procedure developed in the University of Texas at Austin and commonly referred to as TexSARA. The method is mainly divided into two parts and described briefly below. The first part is the solubility-based separation of asphaltenes and extraction of maltenes. The second part is chromatography-based fractionation of maltenes into saturates, aromatics and resins. The apparatus and materials included the following:

- Laboratory balance
- Vacuum manifold:
- Vacuum pump
- Drying oven (preferably with nitrogen purge capability)
- Solvent trap
- A Magnetic stirring plate
- Magnetic stirrer bar
- Wide-mouth round bottle with septa closure
- Silicone strip,
- Metal measuring spoon
- Blunt tip pipetting needle 4-6 inch in length
- Pipettes with 0.1 mL resolution that can be used with the solvents.
- Gloves compatible with the solvents.
- Supplies and consumables
- Sharp/bevel needles, 1.5-2", 20 gauge or higher.
- Syringe filters
- Solid-phase extraction (SPE) cartridges
- Vials with septa top
- n-Heptane
- Toluene
- Dichloromethane (DCM)

- Methanol

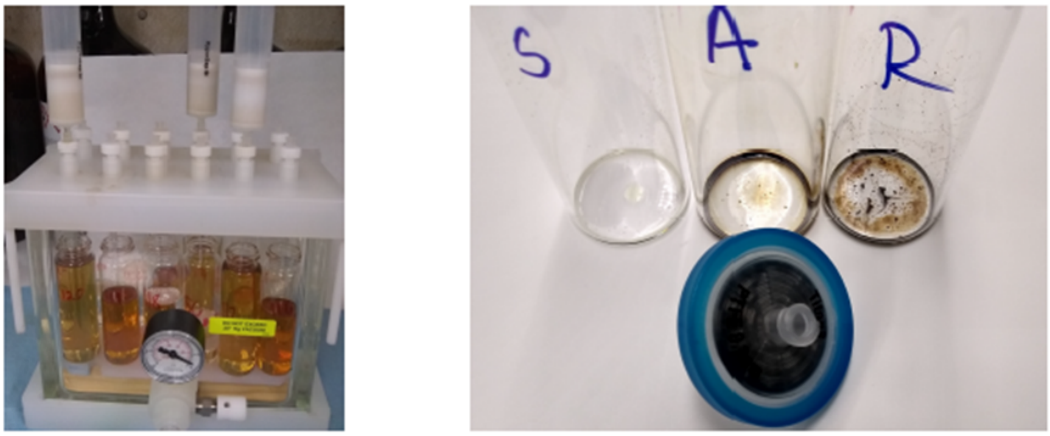
The first part of the procedure entailed the separation of asphaltenes and maltenes. This firstly involved the dissolution of bitumen in n-heptane. This is conducted by placing a small dollop of bitumen (mass~400 mg) in a wide mouth glass mouth with 40 ml heptane. Which is then stirred using a magnetic stirrer for around 24 hours. After mixing, the asphaltenes and maltenes are separated using a PTFE filter (25-30 mm dia, PTFE, 0.2-0.22 μm pore size) under the influence of vacuum, into 4 separately weighed vials. 2 of these vials are then dried under nitrogen purge, and the net mass of the remaining maltenes in the vials are accounted for.

The second part of the procedure is the separation of the maltene fraction into saturates, aromatics and resins. The 3rd and 4th vial from the asphaltene-maltene separation is used for this procedure. Firstly, each vial is diluted with n-Heptane to achieve a 3.33 mg/mL solution, and 15 mL of this solution from each vial is then drawn into separate syringes. Solutions of pure n-Heptane (20 mL and 10 mL in two different syringes or beakers), 80% Toluene- 20% n-Heptane (total 25 mL), and 90% DCM- 10% Methanol (total 40 mL) are then prepared separately in beakers. The steps for the separation into S-A-R fractions are as follows-

- Prepare the vacuum manifold by connecting it to a vacuum source. Place pre-weighed vials (each 40 ml capacity) below the ports and ensure that liner coming from the port discharges directly into the desired vial.
- Mount a fresh SPE cartridge (5 g silica gel, 20 ml capacity) on the pre-wash location of the manifold while keeping the nozzle/vacuum closed. Pour 20 mL of n-Heptane into the SPE cartridge and turn on the vacuum.
- Transfer the cartridge over to the next port/vial for the collection of saturates. Completely close the port nozzle. Introduce 15 mL of maltene-heptane solution from one of the prepared syringes and slowly open the port nozzle to apply vacuum as in the

previous step. When there is no more free liquid at the top of the silica in the cartridge, immediately add 10 mL of n-heptane.

- Transfer the cartridge to the next vial to separate aromatics. Stir and pour 25 ml of the 80% Toluene- 20% n-Heptane solution and apply vacuum as in the previous step
- Move the cartridge to the next vial to separate and collect resins. Pour 40 mL of 90% DCM- 10% Methanol and apply vacuum as done in previous steps. Stop vacuum when the cartridge appears uniform and dry.
- Dry all bottles except pre-wash in the same way as the maltene solution was dried after asphaltene separation process. Weigh the bottles after being cooled and gravimetrically measure the S-A-R fraction using a mass balance. Figure A3.1 shows the final fractionation products after elution and drying



(a) Fractionation products and SPE cartridges after elution.

(b) Collected bitumen fractions

Figure A.4.1 Final fractionation products after elution and drying